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THE JOURNAL
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MOTTLED SILICA BRICK, FACTS, FANCIES, AND FALLACIES*

By Fred A. Harvey and Clyde L. Thompson

Abstract

The extent of coloration is dependent on the amount of lime and alumina and on the thermal history. The coloring agent is usually iron oxide which is present in small amounts. Color is dependent on the grind and on the mixing, drying, and burning procedures. The color can be cleared up or accentuated by controlled laboratory reheating at known temperatures, for definite time intervals. The mottling does not appear unless the brick are well burned. The spots, moreover, have no harmful effect. The literature on this subject is reviewed.

I. Introduction

The subject of mottled silica brick has been of great interest for many years to the user as well as the manufacturer of refractories. The manufacturer has spent much time in the study of the causes of mottling. He knows that mottled brick are normal and just as likely to occur as clear cream-colored brick. It seemed desirable, therefore, to gather together the known facts about color of silica brick and present them in systematic form.

II. Literature Survey

Although the subject of color of silica brick has so long been of interest, the literature on the subject is relatively meager. There are some published articles which represent sound reasoning and some which fail by a considerable margin to agree with the known facts.

One of the earliest observations was that the colored spots, often called liver spots, can be bleached or made to disappear entirely by reburning the mottled brick either in industrial kilns or in laboratory furnaces. Golla[1] mentions this fact, as do McDowell,[2] Phelps,[3] and Rees.[4]

It was originally thought by some that the dark spots were due to relatively high iron content resulting from poor mixing. This fallacy has been exploded, and it has been known for some time that there is very little difference in the chemical compositions of the dark-spotted and light-colored portions of a mottled brick. Careful chemical analyses by Golla[1] showed that there is no more iron oxide in the brown brick than in the light yellow brick. There is sometimes a slightly higher lime content in the dark portions than in the lighter portions although this fact has not been reported by some observers. Lux and Krause[5] mention the higher lime content, whereas Phelps[3(a)] does not mention it. The effect of lime will be discussed more fully.

Shvetsov[6] states that colored spots are the result of high alumina and iron oxide combined with insufficiently high firing temperatures. This statement is entirely fallacious, at least as applied to American-made brick.

There has been some discussion of the relation of apparent specific gravity to color. The apparent specific gravity is definitely related to residual expansion and therefore to the degree of burning, as has been shown by Harvey and McGee.[7]

It is interesting to note that Fig. 5 of this old study shows the bleaching effect of reburning. Golla[1] states that rust-brown spots guarantee normal specific gravity for silica brick. Selzer[8] makes the incorrect statement

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Refractories Division). Received June 25, 1943.

[1] Hans Golla, "Red-Spotted Silica Brick," *Tonind.-Ztg.*, **55** [93] 1285–87 (1931); *Ceram. Abs.*, **11** [5] 311 (1932).

[2] J. Spotts McDowell, "Discoloration of Silica Brick," report of 1925, this issue, pp. 364–67.

[3] (*a*) S. M. Phelps, "Studies of Effect of Chlorine, Sulfur Dioxide, and Carbon Monoxide on Various Refractories," *Amer. Refrac. Inst. Bull.*, No. 9, 8 pp. (1927); *Ceram. Abs.*, **6** [11] 524–25 (1927).

(*b*) S. M. Phelps and E. C. Petrie, "Mottled Silica Brick," revised paper by S. M. Phelps and R. W. Limes, this issue, pp. 378–87.

[4] W. J. Rees, "Mottled Silica Brick," *Bull. Brit. Refrac. Research Assn.*, No. 30, 1933; reprinted in *Trans. Ceram. Soc.* [England], **35** [6] 284–85 (1936); *Ceram. Abs.*, **16** [1] 23 (1937).

[5] Elizabeth Lux and Otto Krause, "Red-Stained Silica Brick," *Tonind.-Ztg.*, **55** [101] 1405 (1931); *Ceram. Abs.*, **11** [5] 311 (1933).

[6] V. N. Shvetsov, "Colored Spots in Silica Brick," *Ogneupory*, **4** [9] 560–65 (1936); abstracted in *Chimie & Industrie*, **38** [2] 303 (1937); *Ceram. Abs.*, **17** [1] 18 (1938).

[7] F. A. Harvey and E. N. McGee, "Testing Coke-Oven Refractories," *Jour. Amer. Ceram. Soc.*, **4** [6] 474–92 (1921); see Fig. 5, p. 487.

[8] Robert Selzer, "Valuation of Silica Brick According to External Nature," *Tonind.-Ztg.*, **56**, 361 (1932); *Ceram. Abs.*, **11** [9] 494 (1932).

that red spottiness, in a particular type of quartzite, is almost always a sign of inferior quality or of light burning. Memnonova and Zil'berfarb[9] state that there is no relation between specific gravity and the color of silica brick. It is true that a well-burned silica brick shows no difference in specific gravity between the dark portions and the light portions of the brick and that mottled brick are found throughout the range of specific gravity of commercially produced brick.

The fact that there is a relationship between the amount of lime present and the color was noted by McDowell,[2] Rees,[10] Golla,[1] Lux,[5] Kalnarskiĭ,[11] and Memnonova.[9] This relation will be discussed in more detail.

The bleaching effect of alumina on color was reported by McDowell[2] and by Golla[1] and will also be covered more fully in this paper.

Harman and Badger[12] claim that the brown color of "flowers" on silica brick can be prevented by the addition of 1% of barium nitrate.

The fact that the surfaces on which the brick rest during drying are less discolored than the other surfaces has been known for a long time and has been mentioned by Golla.[1] Probably starting from this observation, there has been much speculation as to the relation of sulfur in drier and kiln gases to the spotting of mottled brick. Phelps[3(c)] noted discoloration when sulfur dioxide is passed over silica brick at 950°C. (1742°F.), and he mentioned the fact that the color is identical with that which is observed in spotted silica brick. Mellor[13] states, "Discoloration on the surface of lime-bonded silica brick may be produced when the lime is fixed as sulphate by the condensation of dilute H_2SO_4 from the hot kiln gases on the cold brick." Rees[4] states that coal used in firing kilns contains sulfur as sulfide and when the coal is burned the products of combustion contain sulfuric acid and water vapor. Condensation of this acid may occur where the circulation of kiln gases is poor. It will combine with the lime, probably forming calcium sulfate. He believes that the lime sulfate reacts at a slower rate with the silica in the matrix and that the "bleaching" change resulting from the lime-silica reaction is slowed down and a reddish-brown colored skin compound occurs. It seems certain that some relation exists between sulfur in the kiln gases and drier and the mottling of the brick, but the reason given by Rees seems improbable.

One of the "fancies" of the present writers is that the sulfur produces calcium sulfate, which is more soluble than the hydrate, and as the water evaporates from the surface of the brick there is a slight concentration of lime in the portions from which the water is last removed. This slight concentration of lime can cause dark spots if other conditions are favorable.

It is believed that the dark color is due to iron. Inasmuch as there is the same proportion of iron in the white portion of the brick as in the brown, it must be the condition in which the iron exists that causes the color. Lux[5] stated that X-ray analysis established the occurrence of calcium ferrite in crystalline form in red-brown spots. Phelps[3(b)] found that iron is present in both the dark and the cream-colored portions of the brick and that the state of oxidation is responsible for the color. Memnonova[9] observed that pseudowollastonite and calcium ferrite may be observed under the microscope in the dark portions. Birch[14] suggests that lime, silica, and ferrous oxide may form a solid solution of wollastonite and $FeO \cdot SiO_2$, which could undergo an unmixing during burning of the silica brick, thus producing the color.

III. Facts and Some Fancies Influencing Mottling of Silica Brick

In the following discussions of the factors influencing the mottling of silica brick, all variables except the one under discussion are assumed to be constant.

(1) Chemical Composition Factors

(*A*) *Iron Oxide:* Although iron oxide is the coloring agent, variation in the amount in the normal range encountered in American practice has less effect than other factors on the production of mottled brick. It does seem to be true, however, that those ganisters higher in iron oxide are more likely to produce mottled brick. The fact has been established by others and confirmed by the writers that the dark-colored areas of a mottled brick are usually not different from the light-colored areas in the iron oxide content. Microscopic examination of a mottled brick shows minute dark-colored crystals in the matrix of the dark areas that are apparently responsible for the coloration; whether these are iron oxide or a calcium ferrite has not been established by the writers. No such crystals can be found in the light-colored areas, and the iron oxide of these portions must be in solution in a glass or in combination in a silicate mineral.

(*B*) *Lime:* In usual practice, lime is added in the manufacture of silica brick in an amount ranging from about 1.5 to 3.0% of CaO and is an important factor in the mottling or coloration of silica brick. Silica brick made without lime addition are uniformly colored reddish or brown. A small addition of lime bleaches this color, and the brick then have a uniform straw color; further addition of lime results in further bleaching of the color until a lime content is reached at which mottling occurs. The amount required to cause mottling

[9] T. V. Memnonova and L. M. Zil'berfarb, "Spottiness of Silica Brick," *Ogneupory*, **5** [9] 613–15 (1937); Henry Brutcher translation, No. 682; *Ceram. Abs.*, **18** [3] 77 (1939).

[10] W. J. Rees, "Bonding of Silica Brick," *Refrac. Jour.*, **4** [40] 104–109 (1929); *Ceram. Abs.*, **8** [4] 276 (1929).

[11] I. S. Kalnarskiĭ, "Effects of Lime Addition and of Granulometric Composition on Properties of Dinas Brick," *Ogneupory*, **1** [4] 10–15 (1933); *Ceram. Abs.*, **14** [1] 15 (1935).

[12] C. G. Harman and A. E. Badger, "Method of Improving Appearance of Silica Brick," *Brick & Clay Record*, **90** [5] 292–94 (1937).

[13] J. W. Mellor, "Discoloration of Refractories by 'Iron,'" *Trans. Ceram. Soc.* [England], **32** [9] 403–14 (1933); reprinted in *Bull. Brit. Refrac. Research Assn.*, No. 31, June, 1933; *Ceram. Abs.*, **13** [3] 62 (1934).

[14] R. E. Birch, "Phase-Equilibrium Data in Manufacture of Refractories," *Jour. Amer. Ceram. Soc.*, **24** [9] 271–80 (1941).

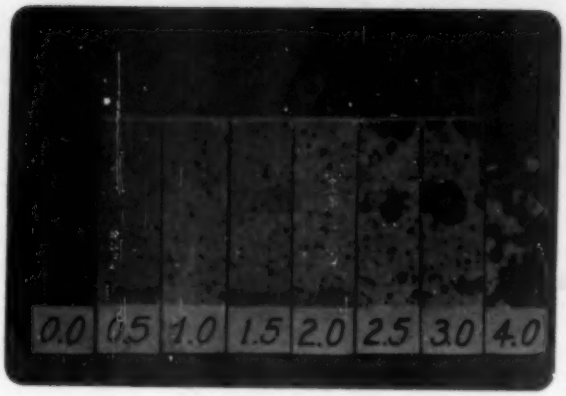

Fig. 1.—Effect of variation in lime.

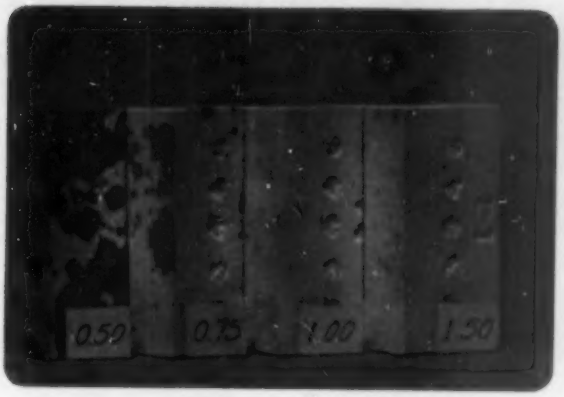

Fig. 2.—Effect of variation in alumina.

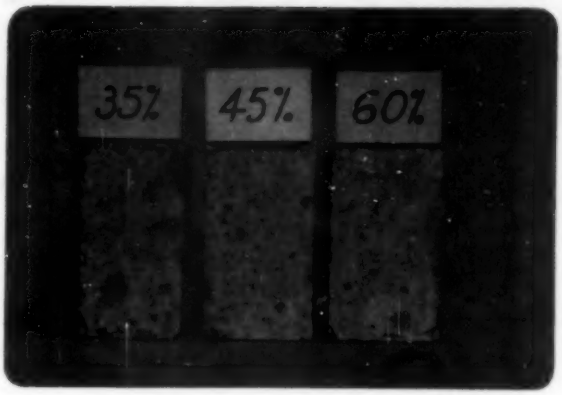

Fig. 3.—Effect of variation in percentage of fines.

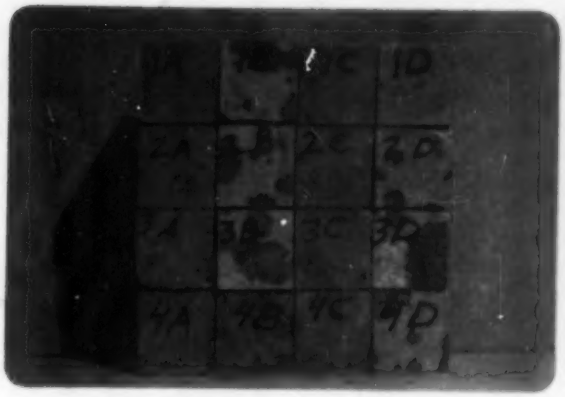

Fig. 4.—Effect of variation in burning treatment.

Fig. 5.—Effect of reheating.

Fig. 6.—Brick after load test.

is dependent on other factors. For an alumina content of 0.75% and normal commercial grinds, mottling is usually encountered at a lime content of between 2.0 and 2.5%. Further lime additions increase the amount of mottling, and the higher percentages frequently produce uniformly brown-colored brick.

This effect of lime is shown in color in Fig. 1. These brick contained about 0.75% of alumina and were of 6-mesh grind with about 45% of −65-mesh material.

(*C*) *Alumina:* Alumina is even more powerful than lime in controlling the mottling of silica brick. If the alumina content is abnormally low, below 0.5%, some of the brick are almost certain to be mottled under normal manufacturing conditions; others may be uniformly colored light brown. A small increase in alumina will reduce the mottling and, with higher alumina content, a very white brick free from spotting is obtained. For those who object to mottled brick, a uniformly colored white brick could be made by using a high alumina rock or by adding a small amount of clay, but it would be inferior in degree of refractoriness.

The effect of alumina on mottling is shown in color in Fig. 2. These brick contained 2.25% of lime and were of about the same grind as those in Fig. 1. It will be noted that there is an agreement in the lime content at which mottling occurs with 0.75% of alumina; this was possible because both lots of brick were made in the laboratory, where all other variables were controlled, and were fired together in a gas-fired kiln.

(*D*) *Sulfur:* Much importance has been attached to sulfur, derived from drier or kiln gases or from sulfite waste liquor used as a bond in the manufacture of the brick, as a factor in the mottling of silica brick. The effect of sulfur has not been systematically investigated by the writers, but because calcium sulfate is considerably more soluble in water than calcium hydrate, its formation could easily cause small irregularities in the distribution of lime on the exposed surfaces of the brick and thus effect mottling. These irregularities would not necessarily need to be of sufficient magnitude to be found by usual analytical methods.

(2) Facts Connected with Manufacture

(*A*) *Grind:* A consideration of the foregoing chemical factors makes it evident that the grind of a silica brick is an important factor in mottling. The lime is added in a finely divided state and acts most readily on the finely ground ganister. Thus an increase in the amount of fines in the brick mix is equivalent to a decrease in lime content and tends to reduce mottling, whereas a decrease in the amount of fines is equivalent to an increase of lime and will increase mottling. This effect is shown in color in Fig. 3. These brick were made of 6-, 8-, and 10-mesh grind with 35, 45, and 60% of pass 65-mesh material, respectively. The brick lowest in fines had much mottling; the intermediate, only a little; and the highest in fines, none. In another series, of which no color photograph is available, the color ranged from large red spots on a uniform light brown background with 32% of −65-mesh material through small red and brown spots on a uniform light-colored background with 39% of fines to a uniform light-colored brick at 47% of fines.

(*B*) *Mixing:* Any irregular distribution of the lime in mixing may result in a brick of nonuniform color, but nonuniformity in color is not proof of poor mixing and any nonuniformity of mixing sufficient to influence the quality of the brick would be readily recognized otherwise.

(*C*) *Drying:* Mottling of silica brick is always more prevalent on exposed faces than on the pallet faces and is probably caused by a little concentration of the slightly soluble calcium hydroxide on the surfaces from which water evaporates. By the same line of reasoning, anything that would cause irregular evaporation of water from the surfaces would be expected to increase spotting. Brick that are dried with hot gases from live kilns show a greater amount of spotting than those dried with gases from cooling kilns, assuming all other conditions to be the same.

(*D*) *Burning:* Mottled silica brick are found throughout the usual range of normal commercial silica brick. Although it is true that underburned brick are not mottled and that mottling can usually be cleared up by continued burning at high temperatures, it is not safe to use color as a criterion of burning. Four brick, each cut into four pieces, were set in four different positions in a commercial kiln. After burning, those in two positions were of a uniform light brown color whereas those in the other two positions had a cream-colored background with large, light brown spots, but each piece had the same apparent specific gravity of 2.32. These are shown in color in Fig. 4. The numbers indicate pieces cut from the same brick, and the letters designate their position in the kiln.

IV. Reversible Nature of Color

It has long been known that mottled silica brick can be cleared up by prolonged heating at a temperature below their original burning temperature and that a uniform cream-colored brick can be darkened by prolonged heating in the range from about 1700° to 2200°F. (925° to 1200°C.). These observations are easily verified; the actual temperature range and time required for these color changes undoubtedly vary somewhat with the chemical composition and other factors that influence the color. The color produced by heating between 1700° and 2200°F. (925° to 1200°C.) is usually uniform, but mottled brick are sometimes obtained in the lower part of the range. This coloration, furthermore, is reversible; it may be cleared up by heating to the higher temperature and restored by heating in the lower range or by slow cooling through this range. This effect suggests that slow cooling of the parts of a kiln in which air circulation is restricted may be a factor in the production of brown-colored and mottled brick in these locations.

Figure 5 shows two silica coke-oven shapes, each cut into three pieces for tests. The center shows the original appearance of the brick, both of which had the normal apparent specific gravity of 2.32. The upper brick, somewhat higher in lime, had a uniform light brown color, and the lower had light-brown mottling

on a cream background. Five hours of reheating at 2550°F. (1400°C.), at least 50°F. below the original firing temperature, changed the uniform brown brick to cream color with small mottlings and removed the spots completely from the one that was originally mottled, whereas five hours of reheating at 2000°F. (1095°C.) merely darkened the brown color of the former brick but changed the mottled brick to a uniform reddish brown.

V. Effect of Mottling on Properties of Silica Brick

Other investigators, particularly Phelps, have established the fact that mottled silica brick are not significantly different from clear cream-colored brick in the properties usually measured such as strength and density. Such data therefore will not be presented here although there are many reports on file to substantiate this conclusion.

Two important properties of silica brick, namely, their ability to withstand loads at high temperatures and their resistance to abrasion, do not seem to have been reported. Mottled and clear silica brick were therefore selected from near the same position in a commercial kiln and tested under a load of 25 lb. per sq. in. until failure occurred. The old schedule for silica brick (C16–20) of the American Society for Testing Materials was used, but instead of holding the temperature at 2730°F. (1500°C.), heating was continued at the same rate to the temperature of failure. Each test included one mottled and one clear brick. The average temperature of failure of three brick of each type was identical, 3050°F. (1675°C.). Two of the brick, after testing, are shown in color in Fig. 6. It will be noted that the mottled brick is still mottled although it has been heated to near its melting point; mottling obviously does not indicate underfiring.

To test resistance to abrasion, the A.S.T.M. paving brick rattler test (C7–30) was used except that the present test was terminated after 600 revolutions. The average weight loss of five lots of mottled brick was 28.2% and that of five lots of cream-colored brick was 29.0%.

VI. Conclusions

The mottling of silica brick is influenced by many factors, both chemical and physical, and the prejudice that still exists in some quarters against mottled brick is not justified. Mottling could be avoided and a very white brick could be produced by the use of ganister containing about 2% of alumina or by the addition of clay to the brick batch, but this process would sacrifice the refractoriness. Such a sacrifice would be decidedly harmful where refractoriness is essential, such as in open-hearth furnaces or electric furnace roofs or glass tank caps. The character of a silica brick depends on its physical properties, workmanship, and performance and not on its color.

Acknowledgment

The writers wish to acknowledge the assistance of the members of the Research Department staff of the Harbison-Walker Refractories Company and particularly that of C. B. Clark, who made the color photographs.

Research Department
Harbison-Walker Refractories Company
Pittsburgh, Pennsylvania

PLANT INVESTIGATION OF VARIABLES AFFECTING COLOR OF SILICA BRICK*

By J. Spotts McDowell

Abstract

The data in this report were obtained during the years of 1923, 1924, and 1925. Among the topics studied were the effects of color in silica brick resulting from the lime, iron oxide, and alumina content of the brick and from varying drying and firing conditions. The effect on color of sulfur gases from coal and the time-temperature relations are also discussed. The lime-alumina ratio, the iron oxide content of the brick, and setting and firing conditions are concluded to be the most significant factors related to the color of the product.

I. Introduction

It has been known for many years that silica brick, which normally come out of kilns nearly white in color with only a minor amount of surface staining, under certain conditions may exhibit spots colored various shades of brown and varying widely in size; or, less frequently, the brick may have a uniformly dark color throughout. In 1923, color of the product from the No. 2 works of Harbison-Walker Refractories Company at Mount Union, Pennsylvania, became a serious matter because many brick were being rejected by inspectors solely on account of color. Observations made at the plant at that time may be summarized as follows:

(1) Various color effects could easily be distinguished from one another through their characteristic appearances. These color effects were (*a*) yellowish-white to cream color, characteristic of well-burned brick from the greater part of the kiln; (*b*) "tobacco juice," the color of a characteristic type of spots, usually of small area; these spots were merely surface stains, and very few well-burned brick were free from them; (*c*) a reddish-brown to chocolate-brown color, which often appeared as "liver spots" on well-burned brick that were otherwise cream colored; this color sometimes affected entire brick; (*d*) a yellowish-brown to reddish-brown color, which appeared in the form of spots generally called "flowering," on a cream-colored background; these spots were intermediate between "liver

* Received June 25, 1943.

spots" and "tobacco juice" in intensity of color, in area affected, and in depth of penetration; (*e*) a light yellowish-brown color, characteristic of underburned brick, affecting the entire brick volume; and (*f*) a reddish tint, associated with a high iron oxide content and occurring in hard-burned brick.

(2) The color that was considered most objectionable by the users occurred in well-burned brick. It was yellowish- or reddish- to chocolate-brown as described under (1) (*c*) and (*d*). It generally occurred in the form of spots of varying size on a cream-colored background, although it sometimes affected entire brick. When the spots were small, the color usually extended only a short distance into the brick; when the spots were large, the dark coloration extended deeply into the brick and affected a large part of the brick volume. Examination of broken brick, however, showed that the percentage of the area affected was almost always greater on the original exterior surfaces than on any interior cross section.

(3) Dark coloration of brick was greatest in the heart of the kiln (the zone in which the brick had been exposed to the peak kiln temperature for the shortest length of time). There was very little spotting of brick which had been set around the sides or near the crown of the kiln or wherever there had been free circulation of kiln gases. Too little draft from any cause, such as tight setting or swinging together of heads, appeared to have favored dark coloration and spotting.

(4) During the unloading of the kilns, it was observed that there occasionally occurred in the setting a zone of dark coloration with a sharp and well-defined border. The border was somewhat irregularly curved and passed from brick to brick in such manner that draft conditions must necessarily have determined its position. Individual brick were seen frequently which were partly outside and partly inside this zone of dark coloration. Such brick were cream colored at one end and either mottled or uniformly dark at the other end.

(5) Dark-colored or spotted brick, reburned with good circulation of air, changed wholly or almost wholly to a yellowish-white or cream color. If they were boxed in during the reburning so that the air supply was limited, they did not lose their dark color.

(6) Shapes having $2^1/_2\%$ or more of lime sometimes fired to a cream color but appeared to be more subject to spotting and dark coloration than shapes containing 2% of lime. Although the amount of lime in the brick appeared to be a factor, a definite conclusion was not reached immediately inasmuch as the high-lime shapes, because of their size, were usually set in the heart of the kiln and in such position that air circulation was somewhat restricted.

(7) One or more spotted brick entirely surrounded by brick of normal color were occasionally seen in the kiln. One brick might be dark in color either partly or wholly, whereas the one next to it and perhaps touching it might be cream colored. This could not be explained by firing or draft conditions.

(8) When the spotting was slight or moderate in amount, there was almost invariably less spotting on the face of the brick which had rested upon the pallet during drying than on the other faces. When the brick were abundantly spotted, the pallet face frequently was as brown as the other faces.

(9) Microscopically, the only noticeable difference between the cream-colored and the darker brick and between the cream-colored and darker portions of the same brick occurred in the matrix. Fettke* reported that the matrix of the cream-colored brick was made up chiefly of tridymite with what appeared to be a colorless lime-silicate glass between the grains; calcium silicate crystals were practically absent. The matrix of the dark-colored brick was likewise made up mainly of tridymite crystals, but between them were seen pale-yellow to yellowish-brown crystals tentatively identified as wollastonite or pseudowollastonite ($CaO \cdot SiO_2$). These crystals were most abundant in brick of darkest color.

Silica brick, which had been partly or wholly dark in color after the initial firing and had become yellowish white after a second firing, then had the same appearance under the microscope as brick that originally were yellowish white.

II. Test Procedure

From the various observations cited, it was concluded that dark colors in silica brick do not result from any single cause but that there are color effects caused by (1) variations in the composition of the brick, (2) drying conditions, and (3) firing conditions. The manufacturing variables which seemed to be possible factors in producing spotting or darkening of color were listed and studied intermittently by plant tests extending over a period of two years. The effect of variations in composition was investigated by manufacturing brick from a series of special mixes by the usual works procedure. Most of the special brick were examined microscopically by Fettke. Only the more important of the variables studied will be discussed here, and for the sake of clarity, these variables will be considered in the order that now seems most logical. This was not the order followed in the investigation.

III. Color Effects Due to Composition of Brick

(1) Effect of Iron Oxide

Fettke's reports indicate that iron oxide in some form was the coloring agent. At that time, however, the iron oxide content of Mt. Union rock was rather uniform, varying only from about 0.60 to 0.95%, and it was not believed that this variation could create such marked effects. Variations in iron oxide therefore were not studied in detail, although brick made from rock containing about 1.25% of iron oxide were found to be considerably redder and darker in color than those made from regular Mt. Union ganister.

(2) Effect of Lime

Analyses showed that the brick that were darkest in color or the most spotted were nearly always high in lime. A brick that had several large chocolate-brown spots was found to contain more than 3.0% of CaO, whereas a light-colored brick made at the same time con-

* C. R. Fettke, Carnegie Institute of Technology, Pittsburgh, Pa.

tained 2.1%. Coke-oven shapes at that time were being made with 2.5% of lime.

Brick were made of special mixes in which the CaO content was varied from 0.5 to 4.0%. After firing, brick containing 0.5% of CaO were not spotted, but they were yellowish brown throughout. Fettke reported that microscopic examination showed the groundmass of these brick to contain numerous small opaque particles, nearly black in color, which formed inclusions in clear, pale crystalline material. The color of the crystals was darkest in the immediate vicinity of the opaque particles. He therefore concluded that the opaque particles, which he considered to be largely or wholly iron oxide, were in the process of going into solution in the crystals at the time the firing was stopped.

Brick containing 1.5 to 2.0% of CaO had the white color, slightly tinged with yellow, which was regarded to be normal for well-burned brick.

With about 2.2% of CaO, some evidence of spotting was observed. The size and number of spots increased with increasing lime content until at 3.5 to 4.0% of CaO the brick were dark brown throughout.

(3) Effect of Alumina

With a lime content of 2%, considerable variation in the amount of spotting was observed, even with brick fired in the same place in the kiln. Some constituent other than iron oxide and lime was therefore assumed also to be a factor.

The alumina content of the rock showed more variation with time than any other constituent. Of fifty analyses made during a two-year period, 20% of the determinations had shown less than 0.6% of Al_2O_3, 20% were above 1.0%, and the remainder was between 0.6 and 1.0%. The average was about 0.8%.

It had been known for a long time that brick high in alumina and containing the normal 2% of lime rarely if ever showed much spotting. Brick were therefore made of a series of mixes in which the alumina content was varied and the lime was held constant; in another series, both the alumina and the lime were varied. The alumina was added in the form of a siliceous clay containing about 20% of Al_2O_3.

Brick low in alumina (under 0.5% of Al_2O_3) and with 2% of lime content were found to be very susceptible to spotting in firing, whereas those containing 0.8 to 1.0% of Al_2O_3 and 2% of lime showed little tendency toward spotting. With 4% of lime and no added alumina, the brick were dark throughout; but with 4% of lime and 0.8% of added Al_2O_3 (total 1.5% of Al_2O_3), they were mainly cream colored with only a few dark spots.

It was concluded that for rock of given iron oxide and alumina content, if cream-colored brick were desired, the percentage of lime in the brick batch must be kept within certain rather narrow limits; with either lower or higher lime content than the optimum amount, dark colors would appear after firing the brick, either in the form of spots on a cream-colored background or affecting entire brick. To produce cream-colored brick with a minimum of spotting from the rock then in use at Mt. Union and having an average Fe_2O_3 content of about 0.8%, it appeared that the lime content should be not less than one and one-half times or more than three times the alumina content.

IV. Color Effects Due to Drying Conditions

(1) Effects of Conditions in Driers

At the Mt. Union plant, the brick were being dried in tunnel driers with products of combustion from the kilns. These gases obviously contained oxides of sulfur as well as of carbon dioxide. There was a general belief at the time of the investigation that sulfur gases, as a result of reactions which took place either in the drier or in the kiln, had a marked effect on the color of the brick.

The lime then as now was being added in the form of calcium hydrate. Analysis of the green brick as they came from the drier showed that at that stage of the process 30 to 70% of the CaO was in the form of carbonate, 1 to 4% in the form of sulfate, and the remainder was still in the form of hydrate. No evidence was obtained which indicated that this small amount of sulfur in the green brick had any effect on the color after firing.

A test of the possible effect of drier conditions on color was made on a full rack car of 9-in. brick. The car was passed through the drier in the usual manner, but instead of being withdrawn when it reached the hot or discharge end of the drier tunnel, it was allowed to stand there for nine days, fully exposed to contact with the kiln gases used for drying. This treatment produced no noticeable effect on the color or on the amount of spotting after firing.

The question has often been asked, "Why do brick that are mainly cream colored almost always show slight surface staining (tobacco juice) and often have dark-colored spots on all faces except the pallet face?" This color may result from the fact that during the drying process moisture from the interior carries some lime in solution and deposits it at or near the surface. This action would increase the percentage of lime as well as the ratio of lime to alumina in these areas.

Attempts to verify this conclusion by analysis have not given entirely concordant results. In the investigation herein described, the lime content of spalls taken from the interior cream-colored portion of a brick was compared with that of spalls from a dark-colored area at the surface and was found to be 0.26% lower. Harvey* has stated that he made analyses of dark- and light-colored portions of brick in which the lime content appeared to be identical. He did not determine the lime-alumina ratios, which appear to be more important than the actual percentage of lime.

V. Color Effects Due to Firing Conditions

(1) Comparison of Brick from Two Plants

At the time this investigation was begun, there was considerable spotting and dark coloration in brick made in No. 2 Mt. Union works and little in those made in No. 1 works. It was assumed therefore that

* F. A. Harvey, Director of Research, Harbison-Walker Refractories Co., Pittsburgh, Pa.

the dark coloration might be due to firing conditions prevailing in the one plant which did not exist in the other. Tests did not verify this assumption because brick made in No. 2 works and burned at No. 1 works came out of kilns spotted and those made in No. 1 and burned at No. 2 were cream colored. The brick made in No. 2 works at that time contained an average of 0.5% more of CaO than those made at the other plant.

(2) Possible Effects of Sulfur Gases from Coal

In the earlier stages of burning, unless there is a great excess of air, the kiln gases may cool sufficiently in the heart of the kiln to reach the dew point and deposit water on the surfaces of the brick. Under these conditions, sulfur gases in the products of combustion would be taken up by the water and immediately react with the free lime in the brick to form calcium sulfate. The possibility that calcium sulfate might influence the color of the brick was therefore considered.

Nine-inch brick were made of special mixes to which plaster of Paris (lime sulfate) had been added. The water content at the time of molding was about 11%. The results indicated that the tendency of brick of high-lime content to become mottled on firing was greater if the lime originally had been in the form of sulfate. With normal lime content, SO_3 appeared to have little or no effect on the color unless it had been present to the extent of about 0.20%. This amount or more of SO_3 appeared to have a tendency to increase the degree of spotting.

The most probable explanation for the effect of SO_3 is based on the fact that calcium sulfate is more soluble than calcium hydrate or calcium carbonate. During the drying of brick containing calcium sulfate, appreciable quantities of the sulfate would be carried to the surface, thereby increasing the ratio of lime to alumina. Although this observation may be true for the special mixes studied, it may have little practical significance.

(3) Time-Temperature Relations

It will be well to repeat some of the foregoing observations in logical sequence. The following comments apply specifically to brick made at the Mt. Union plant of the Harbison-Walker Refractories Company:

(1) Underburned brick are dark in color.

(2) Well-burned brick (cone 18) in the outer portions of the kiln show little tendency toward dark coloration or spotting.

(3) Well-burned brick (cone 18) from the heart of the kiln are frequently more or less spotted, especially if the CaO to Al_2O_3 ratio is high. In this part of the kiln, the final temperature is as high as that at the crown. The bottom of the kiln, however, is the last part to reach the end point of firing, and the brick in the heart and bottom of the kiln consequently are not exposed to the maximum temperature for as long a period as those at the top and sides.

(4) (*a*) Moderately spotted brick, if reburned to cone 18 with free circulation of kiln gases, lose their spots and assume a normal cream color; (*b*) brick that are profusely mottled will clear up to a great extent, but not wholly, if they are reburned to cone 18 with free circulation of kiln gases; and (*c*) spotted brick, which are reset in such a way that the air supply is limited as by boxing-in, do not lose their spots on reburning.

(5) It has also been observed that spotting and darkness of color are greatest in brick from those portions of the kiln having lowest draft or poor circulation of kiln gases. Where there is free circulation, spotting is less likely to occur. It is probable that the temperature is somewhat lower in those portions of the kiln where the flow of gases is impeded than in other portions.

(6) These observations lead to the conclusion that, for brick of normal composition, spotting is largely a time-temperature effect and that probably all silica brick, including those which show no spotting, passed through a uniformly dark condition in the firing process and later through a spotted condition before the final stages of firing were reached.

VI. Works Control

From a standpoint of works control, the most important factors related to color of the product are the setting and the firing. To produce brick of cream color with a minimum of spotting, there should be good circulation of kiln gases and the brick should be burned to cone 18 down. Sulfur gases in the products of combustion passing through the kilns may possibly play a subordinate role in producing spotting. If this should be true, a considerable excess of air during the early stages of firing will minimize the effects of the sulfur gases.

To produce cream-colored brick, the lime content should be carefully controlled and should be neither too high nor too low. If color alone were the determining factor, the best amount of lime for the rock being used should be determined by experiments on color. Color, however, is only one of several factors which must be taken into consideration in deciding the lime content.

Ganister high in iron oxide will produce brick of reddish color. To produce unspotted brick from rock low in alumina, the lime addition should not be greater than the optimum amount. Rock abnormally low in alumina taken from a quarry which also produces rock of higher alumina content should be blended with the latter to maintain a fairly constant average alumina content.

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FACTORS INFLUENCING THE STAINING OF SILICA BRICK*

By L. J. Trostel

Abstract

The staining of silica brick was found to occur in a critical temperature range of 900° to 1000°C. Concurrently the brick had to be "soaked" in this temperature range and exposed to an oxidizing atmosphere. Stained brick could be "cleaned up" or staining prevented by manipulation of the foregoing set of conditions as well as by additions of 4.5% or more of lime. The experimental data examined in the light of the system CaO–Fe_2O_3–SiO_2 suggest that the colorant is the mineral dicalcium ferrite.

I. Introduction

The usual color of fired silica brick is nearly white or light tan. It is well known, however, that the surface or even the interior occasionally may be reddish, deep brown, or liver colored. The latter colors are frequently limited to the surface and take the form of diffused flower-shaped patches. The coloring of the interior, however, may extend to include an appreciable part of the entire volume of the brick. The color of silica brick, in contrast to that of common building brick, is of no importance in the functioning of a furnace constructed of silica brick. In fact, slags and other factors frequently coat or otherwise alter the appearance of silica brick shortly after use. In spite of these facts, some users of silica brick have looked askance at the reddish or brown-colored product. Without questioning the judgment of the user as to whether or not stained brick are less satisfactory in service, refractories manufacturers have incurred considerable expense to supply unstained brick. Phelps,[1] in some careful studies, and those of other investigators[2] have shown, however, that there are no significant differences in the important physical properties of stained and unstained silica brick. The studies of the phenomenon reported in part in this paper explain this fact. The data show that the development of staining occurs under a set of conditions which could have little if any effect on the physical properties of the brick. The temperature range, for instance, in which staining takes place is below that at which any significant percentage of liquid is formed from the matrix material, and it is higher than that required to effect the sudden volume changes associated with the inversions of cristobalite, the chief mineral constituent of the brick.

II. Previous Explanations of Staining

There has been much conjecture as to the mechanism of staining by various observers of the phenomena. Most of these studies have suggested that staining is related in some way to the iron oxide content of the brick, probably because of the predominantly reddish color. The amount of iron oxide in silica brick, however, is so small (1% or less) that positive identification of the iron minerals, even with the microscope, has not been satisfactorily accomplished. The explanations of the cause of discoloration have therefore remained largely in the realm of speculation.

The color has been variously ascribed to extraneous iron introduced during batching by irony water,[2(b)] tramp iron,[2(c)] a fluid iron-sulfur compound,[3] calcium ferrite,[4] or hedenbergite.[5]

The experiments described in this paper were made in order to furnish additional data which, coupled with the findings of previous observers, might provide a better working theory to explain the phenomenon and also determine whether the conditions necessary for color formation were likely to have a deleterious effect on the useful properties of the brick.

III. Outline of Investigation

Laboratory studies were made chiefly on the effect of various atmospheres, such as air alone and mixtures of air with CO_2, CO, and SO_2. This effect was correlated with such factors as time and temperature. Consideration was also given to the concentration of such ingredients as lime and iron oxide, although these normally do not admit of much range in manipulation.

The chief criterion used throughout was the degree of staining. Visual judgment was relied on to measure the relative intensity of color.

These tests were also supplemented by several petrographic examinations and chemical analyses.

IV. Chemical Composition

Representative plant brick of a light tan to cream color from three typical producing districts were used

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* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Refractories Division). Received May 3, 1943.

[1] S. M. Phelps and E. C. Petrie, "Mottled Silica Brick," revised paper by S. M. Phelps and R. W. Limes, this issue, pp. 378–87.

[2] (*a*) R. J. Montgomery and L. R. Office, "Notes on Laboratory Testing of Silica Brick," *Jour. Amer. Ceram. Soc.*, **1** [5] 338–52 (1918).

(*b*) C. G. Harman and A. E. Badger, "Method of Improving Appearance of Silica Brick," *Brick & Clay Record*, **90** [5] 292–94 (1937).

(*c*) W. Hugill and W. J. Rees, "Influence of Iron Oxide and Iron Sulfides on Rate of Quartz Conversion in Commercial Silica Brick Manufacture," *Trans. Ceram. Soc.* [England], **25** [4] 309–13 (1925–1926); *Ceram. Abs.*, **6** [9] 383 (1927).

[3] J. W. Mellor, "Discoloration of Refractories by 'Iron,'" *Trans. Ceram. Soc.* [England], **32** [9] 403–14 (1933); *Ceram. Abs.*, **13** [3] 62 (1934).

[4] T. V. Memnonova and L. M Zil'berfarb, "Spottiness of Silica Brick," *Ogneupory*, **5** [9] 613–15 (1937); *Ceram. Abs.*, **18** [3] 77 (1939).

[5] R. E. Birch, "Phase-Equilibrium Data in Manufacture of Refractories," *Jour. Amer. Ceram. Soc.*, **24** [9] 271–80 (1941).

in the various tests. Their compositions are shown in Table I. These brick were chosen in preference to those of laboratory manufacture because they had been subjected to all of the influences encountered in the usual course of manufacture.

TABLE I
CHEMICAL COMPOSITION OF SILICA BRICK

Constituent	Sample No. 1, Western	No. 2, Eastern	No. 3, Ohio
Ignition loss	0.02	0.02	0.04
Silica	95.24	96.02	95.80
Ferric oxide	0.71	0.42	0.23
Alumina	1.35	1.24	0.99
Lime	2.29	1.96	2.51
Magnesia	0.09	0.15	0.12

Sample No. 1 was used in most of the tests on effect of atmosphere; samples No. 2 and No. 3, differing slightly in Fe_2O_3 and CaO content, were introduced for comparison with sample No. 1.

shape and about one inch in cross section. They were placed in the appropriate muffle furnace while still cold, brought up to temperature, and a slow steady stream of air was blown into the furnace. After being held for varying periods of time they were air quenched by quick withdrawal from the furnace.

Table II shows observations relating to the degree of staining which developed. Staining of a clean brick was developed in a narrow temperature range of 900° to 1000°C. It was necessary, however, to expose the brick six times longer at 900°C. than at 1000°C. to develop the first trace of color. At the higher of these temperatures, staining became progressively worse as the time was increased up to four hours. No staining developed, however, after four hours when the temperature was increased to 1100° and 1200° or after six hours at 1400°. It is worth noting that staining could be produced at 1000°C. in sample No. 3, which had a very low Fe_2O_3 content at 1000°, but it required a much longer time than for sample No. 1, which had approximately three times as much Fe_2O_3.

TABLE II
TESTS OF STAINING IN AIR

Temp. °C.	Exposure time (hr.) 1	2	3	4	5	6	24
600							None
735							None
850						None	
900	None	None	None	None	None	Trace	
935	None	None	Trace	Trace	Trace	Trace	
1000	Trace	Positive	Positive	Intense	Intense	Intense	(*)
1100	None	None	None	None			
1200	None	None	None	None			
1400						None	

* A 24-hr. test at 1000°C. on sample No. 3 showed positive staining.

V. Apparatus for Tests in Various Atmospheres

(1) Two muffle furnaces were used for tests made in ordinary air. For the tests conducted at temperatures ranging up to 1000°C., a wire resistance furnace was used; for tests conducted at temperatures ranging from 1000° to 1400°C., a furnace heated with silicon carbide resistor rods was used.

(2) Two tube furnaces were used for the tests made with mixtures of CO_2 or SO_2 and air. Tests conducted at 1000° C. with CO_2-air and SO_2-air mixtures were made in a wire resistance furnace equipped with a fused silica tube. Tests with SO_2-air mixtures conducted at 1400°C. were made in a gas-heated furnace equipped with an impervious sillimanite tube.

(3) Samples that were exposed to a reducing atmosphere were placed in porcelain crucibles, covered with charcoal, and heated to 1000°C. in one of the muffle furnaces.

VI. Experimental Data

(1) Draw Trial Tests in Air (Oxidizing Atmosphere)

The specimens used in these tests were cut from sample No. 1. The specimens were roughly cubical in

(2) Tests in CO_2-Air Mixtures

Specimens of 1-in. cubes were broken from sample No. 1 and heated for five hours at 1000°C. in a fused silica tube. The specimens were first placed in the cold tube, which was flushed with the particular CO_2-air mixture being tried, and a small steady flow of the mixture was maintained during the complete heating and cooling cycle. The specimens were removed from the furnace at about 400°C.

The observations of the color changes which occurred during the tests are shown in Table III.

TABLE III
TESTS OF STAINING IN CO_2-AIR MIXTURES

Gas mixture (vol.) CO_2 (%)	Air (%)	Free oxygen (in air fraction, %)	Degree of staining after heating at 1000°C.
0	100	20	Intense, reddish color
50	50	10	Intense, olive-drab color
75	25	5	Intense, reddish color
100	0	0	None, bleached gray-white color

The red staining with a concentration of 100% of air was to be expected in view of the results obtained in the draw-trial tests in air. The bleached color which

developed with the 100% CO_2 concentration, however, was unlooked for. It appeared to indicate that the oxygen pressure may be critical. An indication of this pressure range is disclosed by the test, showing that only 5% of free oxygen caused staining.

(3) Tests in Presence of Carbon (Reducing Atmosphere)

Three specimens, (*A*), (*B*), and (*C*), as $^1/_2$-in. cubes taken from sample No. 1, were tested as follows: Specimen (*A*) was placed in a porcelain crucible and covered with pure sugar charcoal; (*B*) was placed on top of the charcoal and a tight-fitting lid covered the top of the crucible; and (*C*), acting as a control, that is, in an oxidizing atmosphere, was positioned on top of the crucible lid.

The specimens as a group were heated simultaneously for 5 hours at 1000° C. in an electric muffle furnace; then, without disturbing them, they were allowed to cool down to about 400° in the furnace and finally were removed.

TABLE IV

TESTS OF STAINING IN REDUCING ATMOSPHERE

Specimen	Observations after heating at 1000°C.
(*A*)	Unstained, gray-white color, somewhat darkened
(*B*)	Unstained, clear gray-white color
(*C*)	Stained throughout, intensely red

Table IV shows the observations of the color which developed. The red color of specimen (*C*) was consistent with that developed in the previous tests when the specimens were heated in the presence of air. The bleached color of specimens (*A*) and (*B*), heated in a highly reducing atmosphere, showed that staining is prevented when the oxygen pressure is lowered sufficiently (as in the case of the specimen heated in 100% of CO_2).

(4) Tests with SO_2-Air Mixture

Specimens of $^1/_2$-in. cubes were broken from sample No. 1 and heated for seven hours, either at 1000°C. in a fused silica tube or at 1400°C. in an impervious sillimanite tube. A gas atmosphere was used, consisting of equal volumes of SO_2 and air. The specimens were first placed in the cold tube and then evacuated to about 10 to 17 mm. of Hg to remove most of the air. The SO_2-air mixture was then introduced and maintained under slight pressure throughout the run and during cooling to room temperature. The effect of moisture was noted, using either moistened gas or moistened samples.

TABLE V

TESTS OF STAINING IN A SO_2-AIR MIXTURE

Temp., °C.	Moisture additions	Color after heating (no staining)
1000	None	Gray-green
1000	Wet gas	" "
1000	Wet brick	" "
1400	Wet brick	Gray

Table V shows the color changes observed during the tests. All of these tests show a consistent lack of staining, similar to that found either in the presence of carbon or in 100% CO_2. The presence of moisture is apparently not important.

(5) Reignition of Bleached Specimens

The lack of staining (in fact, actual bleaching) developed in certain types of low-oxygen atmospheres in these tests led to the belief that at 1000° and with the proper time of exposure all silica brick of normal composition are potentially capable of staining but that the mineral colorant which forms requires a certain oxygen pressure to form a visible stain. It was decided, therefore, to reignite some of the bleached specimens in an oxidizing atmosphere. The length of the heating period and the temperature were purposely made less than the minimum at which staining had been found to take place in air in previous tests.

Specimen (*A*) from the reducing atmosphere test and all specimens from the SO_2-air tests were ignited for $^1/_2$ hour at 800°C.

Intense red staining developed throughout each specimen except one as the result of this treatment. This exception was the specimen formerly heated to 1400° in the SO_2-air mixture, and this temperature, it will be remembered, was incapable of producing staining even in the tests in air.

Whatever the coloring mineral may be, it apparently is not stable under the test conditions at temperatures as high as 1400°C. Although it seems quite evident that the mineral forms at 1000°C., it is not apparent unless the brick are heated in the presence of sufficient oxygen. The latter observation suggests that the coloring mineral is a compound containing ferric iron.

(6) Removal of Staining

The previous tests on unstained sample No. 1, heated in the range of 1100° to 1400°C. in air, failed to develop staining, which was an indication of the instability of the coloring mineral at these temperatures. Previous investigators have pointed out that staining could be removed by reburning at elevated temperatures. This reburning has been common practice by silica brick manufacturers to "clean up" stained brick where customer prejudice exists.

To verify the results of reburning and to locate a little more closely the temperature required to eradicate the staining, several tests were made by heating in air two specimens of stained brick; sample No. 1 was tobacco colored, and sample No. 2 was bright red. Temperatures of 1200° and 1400°C. were chosen (see Table VI).

TABLE VI

EFFECT OF REBURNING STAINED BRICK IN AIR

Specimen No.	Conditions of test: Time (hr.)	Conditions of test: Temp., °C.	Observations after heating
1	7	1200	All stain removed
1	7	1400	" " "
2	7	1200	" " "
2	7	1400	" " "

Table VI shows that reheating for seven hours to only 1200°C. was sufficient to clean up the comparatively small specimens of silica brick. The time and temperature required for this purpose in commercial kilns with their large settings, of course, may be somewhat higher. Mere reheating of the brick is no guarantee that they will stay clean as shown by a further test on specimen No. 1 after the 1400° reheating. This specimen was again heated for seven hours at 1000°C. in air, and the staining reappeared as a red color but was much more intense throughout.

(7) Effect of Increased Lime on Staining

The foregoing work established the effect of atmosphere and the approximate time and temperature necessary to develop staining, but another factor was considered to be important in this investigation, namely, the concentration of certain of the brick components, such as lime and iron oxide.

The tests in air shown in Table II on samples No. 1 and No. 3, containing 0.71 and 0.23% of Fe_2O_3, respectively, showed that staining occurs in the presence of comparatively small percentages of this oxide. The effect of varying lime content in the brick mix, however, was unknown.

Mixes of silica brick, accordingly, were made up in which the lime content was so increased as to exceed that used in normal practice. The iron oxide content was held constant and corresponded to sample No. 2. The brick were burned in a plant periodic kiln to cone 17, and color observations were made after burning.

A part of each brick was then reheated for $5^1/_2$ hours in air at 1000°C. to determine whether any of the unstained brick were potentially capable of staining because the kiln treatment covered a variety of time, temperature, and atmospheric conditions not under precise control.

The observations made after burning in the kiln and after reheating are shown in Table VII.

TABLE VII

BRICK OF VARYING LIME CONTENT

Lime in mix (%)	Color	
	After burning to cone 17	After reheating in air at 1000°C.
2.5	Red mottling on all surfaces; otherwise nearly white	Staining increased
4.5	No staining	No staining
6.5	" "	" "

In spite of the fact that all mixes of the brick were exposed in the reheat test to the proper time-temperature-atmospheric conditions to produce staining, only the mix of 2.5% of CaO exhibited discoloration. This latter fact suggests that there is a critical range of lime, which if exceeded prevents discoloration of the brick. The determination of the exact boundary limits of this range was not further investigated because the minimum lime content of the silica brick being tested cannot be exceeded to a great extent without adverse effects on the brick properties.

(1943)

(8) Petrographic Examination

From an examination of a thin section of a typically reddish, flowered surface stain of a silica brick, the red color was found to be localized in the groundmass or fine fraction. Wollastonite was the predominant matrix material of the groundmass. Because of difficulties encountered in the identification of the very small amounts of colored phases involved, Bowen* kindly examined some of the stained material. He found that the wollastonite contained what appeared to be some dicalcium silicate formed as an initial phase in the reaction between lime and silica and not yet completely transformed to wollastonite. The red patches contained minute channels of an orange-colored glass from which crystals of high birefringence and high extinction had formed.

Other examinations of stained brick by the author have shown the presence of minute red crystals of dendritic habit arranged in parallel groups but with the orange-colored glass absent. In stained brick, which had been decolorized by exposure to a reducing atmosphere, the crystals maintained the same structure but the red color had changed to black.

Because of the very small size and quantity of these crystals and the practical difficulties of freeing them from the inclosing silicate phase, optical measurements of their properties were difficult and very limited. Inasmuch as the lime added to the brick mix is concentrated in the groundmass, it is logical to assume that lime is an essential component of the colored mineral phase. It was not possible, however, to determine from the petrographic examinations exactly whether the reddish-colored phase was hematite, calcium ferrite, or an oxidized iron silicate.

VII. Discussion of Data

Without venturing to suggest the exact mineral which causes staining, it is possible to summarize the conditions that were found to be necessary to cause its appearance.

Only very small amounts of iron in the brick are required, and its formation is inhibited above certain limiting amounts of lime. Of much interest is the fact that the discoloration is caused by a ferric iron mineral, although the staining may be masked in an atmosphere of very low oxygen concentration. It is evident that the staining is not the result of a change in chemical composition during burning other than in the oxygen ratio of the iron compounds, since the phenomenon could be made to appear, disappear, and reappear merely by manipulation of certain physical conditions.

A temperature of about 1000°C. is a necessary condition, whereas temperatures of 1200°C. and above temporarily destroy the mineral. Time of heating is also a necessary corollary. When the amount of iron was very low (0.23%), for instance, the time required to produce staining was found to be as long as 24 hours. This effect is in contrast with the case in which the iron content was much higher (0.71%) and only one hour was required.

* N. L. Bowen, Department of Geology, University of Chicago, Chicago, Ill.

Because the colorant is probably a ferric iron compound, its presence might be explained by an inspection of the system CaO–Fe_2O_3–SiO_2. Dicalcium ferrite, in this system, has been suggested by other investigators to be the colorant. Its presence would have to be correlated with that of wollastonite, a common constituent of the groundmass of silica brick. The join between the compounds $2CaO \cdot Fe_2O_3$ and $CaO \cdot SiO_2$ investigated in connection with the composition of Portland cement by Burdick,[6] Iwase and Nisioka,[7] and Sitz,[8] is of special interest in this connection. The eutectic temperature for mixtures of $CaO \cdot SiO_2$ and $2CaO \cdot Fe_2O_3$ containing from 50 to 90% of the former is, for example, about 1180°C. This is rather close to the critical temperature at which staining could be made to appear or disappear. Alumina, one of the constituents of silica brick, is also likely to be present in the eutectic mixture. The actual eutectic temperature in a brick would thus probably be somewhat lower than for the simple binary $2CaO \cdot Fe_2O_3$–$CaO \cdot SiO_2$.

In the petrographic examination of some of the stained brick, it will be remembered that an orange-colored glass was found from which minute reddish crystals were growing, although they could not be positively identified. This structure, considered in conjunction with other facts developed in this investigation, suggests that the stained areas represent a partially devitrified eutectic composition with incipient growth of dicalcium ferrite.

The present experiments, interpreted in terms of the foregoing theory, therefore mean that the red- or brown-colored ferrite will appear if the eutectic is devitrified by heating long enough under the eutectic temperature (at about 1000°C.) and, of course, in an oxidizing atmosphere. If the temperature is raised to about 1200° C. and above and held long enough, the ferrite redissolves and the color disappears. The liquid so formed, containing among other things appreciable amounts of the ferrite, would have comparatively high fluidity, which was noted by Sitz[8] and was also suggested by the work of Endell, Heidtkamp, and Hax.[9] This effect could account for the diffused or flower-shaped patterns typical of stained brick. Even if the ferrite, presumed to be present, had been formed by the proper time-temperature conditions, it could be masked out by changing the iron from the ferric to the ferrous condition and it could be made to reappear on reignition at low temperatures (well below that of the eutectic).

If the eutectic must be "soaked" to devitrify it and to produce staining, it is logical to inquire how rapidly the brick must be cooled to prevent devitrification. The data are not comprehensive enough to indicate this rate with complete assurance. From certain cooling data taken in the course of the experiments, it is known that no staining developed when the particular brick used were cooled from temperatures near the critical range (1000°C.) and at rates varying from 18.3° to 5.5°C. per minute. These rates are to be contrasted with much slower rates of 0.12° to 0.22°C. per minute at comparable temperatures measured in the ordinary operation of periodic silica brick kilns. Although these latter rates were not measured in connection with staining, they are typical of those encountered in usual plant practice when staining does sometimes occur. Merely refiring brick above the critical temperature, therefore, is not a permanent cure for staining because it may reappear if the rate is too slow on the next cooling.

The fact that a brick has escaped staining during regular burning, moreover, is no guarantee that it cannot be stained later, as the present tests have shown. It would thus be expected that brick would become stained after use in furnaces where certain zones are maintained under oxidizing conditions and at about 1000°C. for long periods of time. Experiences with certain portions of coke-oven structures made of silica brick actually show this phenomenon.* For instance, on dismantling the regenerator walls of ovens, a zonal staining is frequently noted in the form of a band of red-colored brick starting at a point 4 to 5 feet from the bottom of the regenerator and extending upward a distance of 3 to 4 feet. At this height, the temperatures exceed 1038° to 1093°C.

The role of the sulfur gases in the kiln atmosphere, always debatable heretofore, can now be explained with a little more certainty. It is well known[10] that at temperatures as low as 700° to 800°C. Fe_2O_3 is reduced by SO_2 to Fe_3O_4. The red or brown color typical of a mineral containing Fe''' thus would not appear in the presence of SO_2. This effect is in line with the present tests, which showed that brick did not stain when they were held at the critical temperature and then cooled in a reducing atmosphere. Under such conditions, the brick were a gray-white or gray-green color, which, of course, is not the normal color of either clean or stained commercial brick. The clean brick are generally a light cream to tan color, suggesting that kiln atmospheres are nearly always oxidizing during the cooling cycle.

In the laboratory tests recorded in the literature in which silica brick were stained after exposure to temperatures of about 1000°C. and to SO_2 gas, the staining was probably the result of air infiltration in

[6] M. D. Burdick, "System Lime–Ferric Oxide–Silica," *Jour. Research Nat. Bur. Standards*, **25** [October, No. 4] 475–88 (1940); R.P. 1340; *Ceram. Abs.*, **20** [2] 57 (1941).

[7] Keizo Iwase and Usaburo Nisioka, "Equilibrium Diagrams of Three Binary Systems, (1) $CaO \cdot SiO_2$–TiO_2, (2) $CaO \cdot MgO \cdot 2SiO_2$–$MnO \cdot TiO_2$, and (3) $CaO \cdot SiO_2$–$2CaO \cdot Fe_2O_3$," *Science Repts., Tôhoku Imp. Univ., Series 1*, **26** [4] 592–601 (1938); *Ceram. Abs.*, **17** [11] 365 (1938).

[8] G. Sitz, "System CaO–Fe_2O_3–SiO_2 in Relation to Its Significance for Metallurgical Slags," *Metall Erz*, **29** [13] 269–76 (1932); *Ceram. Abs.*, **11** [12] 639 (1932).

[9] Kurd Endell, Günther Heidtkamp, and Ludwig Hax, "Über den Flüssigkeitsgrad von Kalksilikaten, Kalkferriten, und Basischen Siemens-Martin-Schlacken bis 1625°," *Arch. Eisenhüttenwesen*, **10** [3, September] 85–91 (1936); *Ceram. Abs.*, **16** [1] 46 (1937).

* W. C. Rueckel, Koppers Company, Pittsburgh, Pa., personal communication.

[10] O. C. Ralston, "Iron Oxide Reduction Equilibria," *Bur. Mines Bull.*, No. 296, 326 pp., 1939; p. 8.

the furnace while the brick were cooling after the SO_2 flow was shut off.

Acknowledgment

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INFLUENCE OF WATER VAPOR ON SILICA BRICK AT HIGH TEMPERATURES*

By Fred A. Harvey

Abstract

Some tests are described which show that water vapor does not cause softening of silica brick at a temperature of 2900°F. in a sixteen-hour laboratory test.

I. Introduction

A recent project important for national defense required that the refractories used should be unaffected by steam at high temperatures. The other properties required of the refractories were such that silica brick were suitable. An article by Dodd,[1] however, indicates that silica brick are strongly affected by water vapor at temperatures between 1500° and 1600°C. (2732° to 2912°F). Because the question was important, it was decided to try to check his conclusion. Dodd states that his work was suggested by a failure in an open-hearth roof, which showed some resemblance to the "rotting" effect that is found in silica brick when water finds its way into an open-hearth furnace structure during repair. Although the major cause of the failure was found later to be more intimately connected with the working of the furnace, the results of his tests on the action of water vapor are considered to be of general interest.

II. Review of Dodd's Work

Dodd used a Hirsch-type test furnace, which is commonly used in England for the refractoriness test. Edwards[2] has presented a discussion of this furnace. It is an electric tube furnace with granular carbon resistor. Temperature control is difficult, and local hot spots are not unusual. It is hottest in an annular ring near the center of the tube of the furnace. Dodd used a metal tube, which led steam into the lower end of the furnace and was luted in position with a clay mixture to form as tight a joint as possible. Cracks which formed during a test were sealed with clay. The silica brick test pieces, in most cases, were cut from 12-in. open-hearth roof brick. The dimensions of the test pieces were not reported, but it was stated that they were ground to an elliptical cross section. The test piece was suspended in the tube of the furnace by means of a Nichrome wire fastened to an iron rod which rested on the furnace casting. It was thus possible to rotate the specimen from time to time to eliminate the effects of hot spots on one side of the furnace and irregularities in the shape of the test piece. The gap between the sillimanite furnace tube and the test piece varied from $\frac{1}{2}$ to 1 in.

The rate of heating was rapid for silica brick, 400° to 500°C. per hour, up to dull redness. The temperature was raised from 800° to 1500°C. in an hour and then held between 1500° and 1600°C. until the specimen broke; this occurred in a period varying from 20 minutes to four hours. Dodd states that this was done in an attempt to reduce the risk of spalling and to avoid condensation of water vapor. He found that when a temperature of 800°C. was reached the temperature of the whole furnace exceeded 100°C. and the greater part of the furnace was above the critical temperature of water vapor. It should be noted that there may have been a temperature difference of nearly 700°C. between the center and ends of the test piece and that the test piece was heated from room temperature to 1500° or 1600°C. in about $2\frac{1}{2}$ to 3 hours. He does not describe the method used for measuring temperature, and it is evident that it would be difficult to measure accurately the temperature of a test piece hanging in and nearly filling a vertical tube, particularly when the center is much hotter than the ends. In a discussion of the paper, Rees[3] asked whether Dodd was quite clear on the accuracy of his temperature measurements "as on one piece there is serious deformation and actual fusion. There is evidence on one side of the test piece of localized heating, which is difficult to avoid with the Hirsch type of furnace."

Dodd reported that he carried on a "blank" test, keeping the temperature conditions identical with those of the first test but allowing air to pass through the furnace in place of water vapor, and that this specimen was unaltered. He does not state whether he made a blank test for each type of brick tested or merely for one brick. The text implies that only one test was made.

Nine brands of silica brick were tested and all failed in 20 to 240 minutes. Figure 1 shows the appearance

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Refractories Division). Received April 10, 1943.

[1] A. E. Dodd, "Action of Water Vapor on Silica Brick at High Temperatures and Its Possible Industrial Significance," *Trans. Ceram. Soc.* [England], **35** [5] 223–46 (1935–1936); *Ceram. Abs.*, **16** [7] 206 (1937).

[2] Cyril Edwards, "Notes on Testing of Refractory Materials," *Trans. Ceram. Soc.* [England], **33** [7] 260–73 (1933–1934); *Ceram. Abs.*, **14** [4] 95 (1935).

[3] W. J. Rees, "Discussion of Dodd's Paper," *Trans. Ceram. Soc.* [England], **35** [6] 244 (1935–1936).

FIG. 1.—Typical examples of the two types of failure.

of two of the broken specimens. Specimen *A* may be the one mentioned by Rees that showed signs of fusion. Dodd says that Fig. 1 shows typical examples of the two types of failure found. Specimen *A* appears to have been quite viscous during treatment and to have failed by pulling into two pieces from the weight of the lower portion. He also states that specimen *B* failed with little sign of fusion but appears to have been rotted by the water vapor. If specimen *A* refers to the *A* given in Table I (see Table I taken from Dodd's paper), it had 0.98% of alumina and the very high value of 1.16% of alkalis. Specimen *B* shows 2.60% of alumina and 0.6% of alkalis. These values indicate that the specimens were decidedly low in refractoriness according to American standards. Specimen *A* would be expected to soften or melt at a temperature not much above 1600°C., and it would be quite fluid at a temperature below 1650°C. (3002°F.).

The remaining part of Dodd's paper contains an extended description of each test piece examined both macroscopically and microscopically before testing. There is also a study of the literature on the nature and action of water vapor at high temperatures. Dodd's conclusions are stated as follows:

1. A high Fe_2O_3 content causes failure in an atmosphere of water vapour, probably due to hydrolysis rather than to reduction.
2. A low lime content also appears to accelerate failure.
3. Some volatilisation of silica, with immediate deposition in the amorphous form, would account satisfactorily for the rotting effect.
4. Water vapour causes a marked decrease in the viscosity of the bond, either by solution, by chemical action, or a combination of both.

A study of Dodd's paper leads one to believe that his conclusions are not very convincing. The actual temperatures reached by the specimens are not stated exactly and may have been locally higher than 1600°C. It is not stated whether blanks or control tests (without steam in the furnace) were run on all the brick tested or merely in one case. The chemical analyses, furthermore, indicate rather low-quality silica brick.

III. Further References

Parmelee and Westman[4] found no evidence that steam reduces the transverse strength of fire-clay brick up to temperatures of 1100°C. German,[5] moreover, found little or no effect of steam on the structure or mechanical resistance of silica brick for coke ovens up to 1150°C. Badger[6] showed that water vapor accelerates in a marked manner the rate of vitrification of some ceramic bodies which contain notable amounts of feldspar. These tests were carried out at temperatures of about 1170°C. in a laboratory furnace and at cone 7 in an oil-fired kiln. Possibly the unusually high alkali content of Dodd's specimen *A* would render it susceptible to the action of water vapor, whereas silica brick of normal low flux content would not be affected.

Most furnaces have an appreciable amount of water vapor present at all times in the products of combustion. Table II, for example, gives a calculation of the composition of the kiln atmosphere in laboratory furnaces fired with natural gas (*a*) with theoretically perfect combustion and (*b*) with 10% of excess air, which is close to normal testing conditions used at the Harbison-Walker Refractories Company Hays Laboratory.

[4] C. W. Parmelee and A. E. R. Westman, "Effect of Steam on Transverse Strength of Fire-Clay Brick," *Jour. Amer. Ceram. Soc.*, **10** [4] 292–98 (1928).

[5] S. L. German, "Effect of Steam on Silica Brick for Coke Ovens," *Ukrain. Nauch-Issledovatel. Inst. Ogneuporov & Kisloptouporov*, No. 45, pp. 120–22 (1939); *Ceram. Abs.*, **19** [3] 67 (1940).

[6] A. E. Badger, "Effect of Various Gaseous Atmospheres on the Vitrification of Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **16** [2] 107–17 (1933).

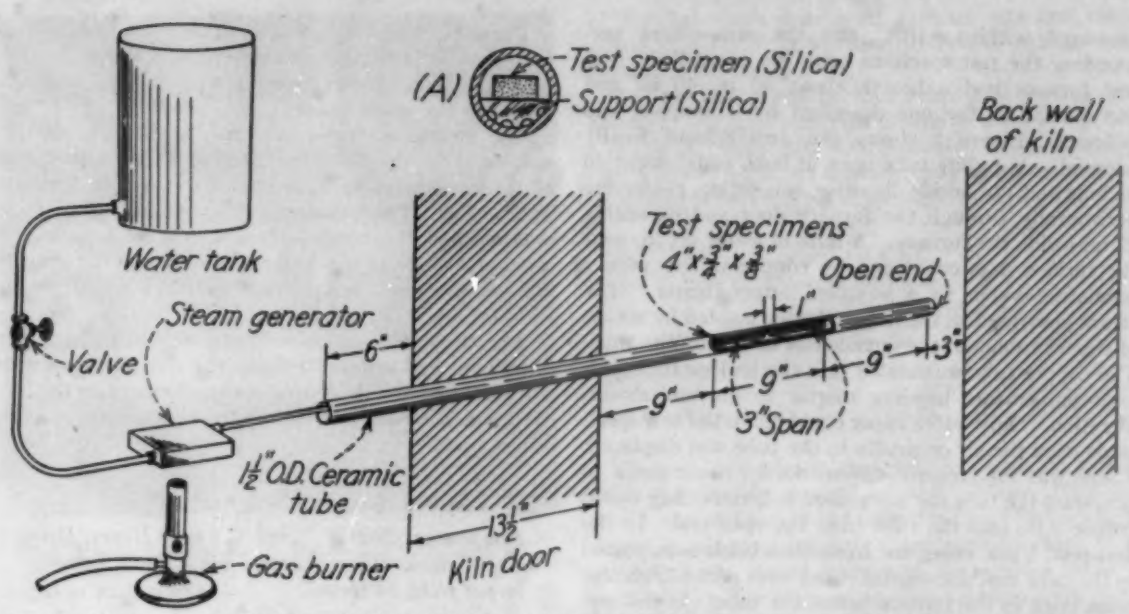

FIG. 2.—Steam treatment of silica brick at 2900°F. (A) Enlarged section through ceramic tube showing test specimen and detail of support.

TABLE I*

Mark	A	B	C	D	E	F	G	H	I
Analysis									
SiO_2	95.30	94.01	95.51	94.60	94.30	94.02	94.28	94.52	95.31
Al_2O_3	0.98	2.60	1.48	1.97	1.51	1.80	1.68	1.50	0.99
Fe_2O_3	0.86	0.40	0.88	0.43	0.29	1.12	1.04	1.42	0.80
CaO	1.90	2.05	1.48	2.20	2.50	1.60	1.52	1.72	1.70
MgO	0.12		0.10			0.21	0.23	0.12	0.21
Alkalis	1.16	0.60	0.90	0.66	0.53	0.78	0.53	0.42	0.50
Ordinary refractoriness	1730°	1700°	1710°	1700°	1710°	1710°	1730°	1700°	1730°
Porosity (%)	21.2	28.0	25.5	27.7	26.7	23.8	29.2	27.4	25.6
Permeability (c.g.s. units × 10^8)	8.8	163	54	114	216	108	255	100	183
Class of pore†	Very small	Medium–large	Small–medium	Medium	Large	Medium–large	Large	Medium	Large
True density	2.39	2.32	2.51	2.33	2.33	2.325	2.32	2.32	2.35
Apparent density	1.88	1.67	1.86	1.68	1.71	1.77	1.64	1.68	1.75
Time (minutes) before failure in "steam test"	70	90	60	180	240	25	20	20	65

* From Dodd (see p. 226 of footnote 1).
† The class of pore is determined from the porosity and permeability data according to the method of Easter.

If water vapor in concentrations up to 18% caused a marked lowering of the refractoriness of silica brick, it could not have escaped observation in either the testing or industrial furnaces. A comparison of the temperature of silica roof brick in open-hearth steel furnaces and in electric steel furnaces, for example, would disclose any marked difference in refractoriness.

Comparative load tests on some special silica brick, which have been conducted in a natural gas-fired furnace at Hays Laboratory and in an electrically heated furnace at the Electrotechnical Laboratory* at Norris, Tennessee, show that there is no definite difference between the results of the two laboratories. The gas-fired furnace atmosphere, however, contained about 17% of water vapor and the electrically heated furnace atmosphere contained only traces.

TABLE II
COMPOSITION OF KILN ATMOSPHERE (%)*

	(a)	(b)
CO_2	9.9	9.1
H_2O	18.4	16.9
O_2		1.7
N_2	71.7	72.3
Co_2, dry basis	12.1	11.0

* Based on gas analyses furnished by the Equitable Gas Co., Pittsburgh, Pa.

IV. Description of Tests

To find a definite answer to the question of whether water vapor lowers the strength of normal silica brick, a test was devised in which the temperature could be

* Hewitt Wilson, Supervising Engineer, Electrotechnical Laboratory Bureau of Mines, Norris, Tenn., personal communication.

measured within ±10°C. and the atmosphere surrounding the test specimen could be controlled. The test furnace had a hearth about 30 by 40 in. and was similar to the one described by Thompson and Wilcox.[7] Figure 2 shows the arrangement finally adopted. A mullite tube open at both ends, about 46 in. long and 1 in. inside diameter, was set up, projecting horizontally through the furnace door and extending 27 in. inside the furnace. A tank of water set up near the furnace was connected by copper tubing with a regulating valve to a so-called Super-Heater. The steam generated in the Super-Heater was led by means of copper tubing to the outside end of the mullite tube. The copper tube was sealed into the mullite tube with high-temperature bonding mortar to prevent air infiltration. Only water vapor could reach the test specimens once the air originally in the tube was displaced. There was no pressure differential to cause gases to penetrate the tube nor any reason to believe they would diffuse 9 in. into the tube from the open end. In the first test, 3/4-in. cubes cut from silica brick were placed in the tube and the control cubes were set on high alumina brick in the furnace beside the tube. In the second and third tests, bars, 4 by 3/4 by 3/8 in. cut from the same silica brick, were supported inside the tube so that they had a free span of 3 in. Any softening of the bars would have resulted in sagging. A short section of tube, open at both ends, was placed beside the long tube inside the furnace. This tube contained a second bar set up in the same manner as the test specimen and used as a control test in tests Nos. 2 and 3. Three separate test runs were made, the first at 2700°F. (1482°C.), and the others at 2900°F. (1593°C.). The temperature was measured by means of a platinum-platinum 10% rhodium thermocouple and a Leeds and Northrup continuous recorder. A Rayotube, focused on the inside of the furnace and connected to a Leeds and Northrup Micromax recorder, was also in continuous operation during the tests as a second check on constancy of temperature.

It is known from frequent check testing that the temperature of this furnace is uniform within about ±10°C. over the hearth.

Typical chemical analyses for the two types of silica brick tested are shown in Table III.

(1) Test No. 1

Temperature 2700°F. (1482°C.) for 5 Hours, Using Tap Water as the Steam Source; Time to Reach Temperature of Hold, 12 Hours

In the first test, 3/4-in. cubes cut from brick made (*a*) of Medina quartzite by the power-press process, (*b*) of Medina quartzite by the drop-machine process, and (*c*) of Baraboo quartzite by the power-press process were set in the tubes. The pieces were weighed before and after the test, using a beam balance accurate to about ±0.02 gm. The differences in weight before and after steaming were so slight as to be within the limits of experimental error (Table IV).

[7] C. L. Thompson and H. G. Wilcox, "High Temperature Gas-Fired Test Furnace," *Bull. Amer. Ceram. Soc.*, **19** [9] 336–37 (1940).

Pieces Nos. 1, 2, 5, 6, 9, and 10 were used as controls and were set on high alumina brick. Pieces Nos. 3, 4, 7, 8, 11, and 12 were placed within the tube and subjected to the water vapor.

The steam generator was run at 440° to 460°F. measured at the discharge end, and steam from tap water was started through the tube when the kiln was at 2550°F. The maximum temperature of the test was reached 1 1/2 hours later and held for 5 hours. A total of 2000 cc. of tap water was used, and the average temperature for 5 hours was 2703°F. with a maximum of 2710°F.

The steam-treated pieces were bleached and had a slightly glazed surface, whereas the control pieces were not bleached and no glazing occurred except on the bottom, which was in contact with the high-alumina setting shape.

(2) Test No. 2

Temperature 2900°F. (1593°C.) for 5 Hours, Using Tap Water as Steam Source; Time to Reach Temperature of Hold, 14 Hours

In the second test, bars 4 by 3/4 by 3/8 in. and their supporting shapes were cut from the same brick used in test No. 1. The supports were cemented to the test bars with Canada Balsam so that the specimens could be inserted into the tube and the 3-in. span could be maintained. The control specimen was of brick made of Baraboo ganister. Steam was first introduced at

TABLE III

CHEMICAL ANALYSES OF SILICA BRICK

	Brick sample	
	Medina quartzite (%)	Baraboo quartzite (%)
SiO_2	96.80	96.00
Al_2O_3	0.94	1.09
Fe_2O_3	0.53	0.60
CaO	1.92	2.52
MgO	0.08	0.03
Alkalis	0.25	0.11
Total	100.52	100.35
Apparent specific gravity	2.32	2.34

TABLE IV

TEST NO. 1

Sample No.	Weight (gm.) Before	After
	Eastern power press	
1	26.20	26.16
2	24.16	24.13
3	22.60	22.61
4	22.42	22.38
	Eastern drop machine	
5	24.67	24.67
6	23.34	23.34
7	22.91	22.89
8	21.66	21.65
	Baraboo power press	
9	28.83	28.83
10	28.33	28.32
11	26.66	26.65
12	27.20	27.19

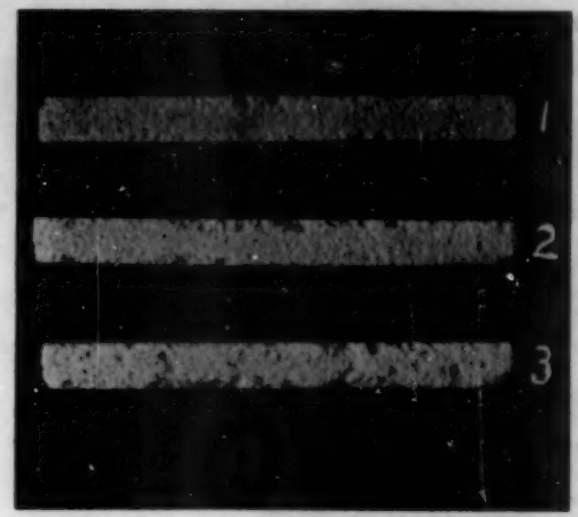

FIG. 3.—Test bars: No. 1, blank, not steamed; No. 2, from Baraboo rock; No. 3, from Medina rock; both subjected to water vapor.

2600°F. 1 hour and 45 minutes before the hold was reached The average temperature of the 5-hour hold was 2893°F. and the maximum, 2900°F. A temperature range of 520° to 550°F. was maintained at the discharge end of the steam generator. A total of 3100 cc. of tap water was used.

None of the silica slabs showed any bending. The steamed pieces were slightly glazed and considerably bleached in the same manner as the cubes that were tested at 2700°F. The control bar showed no bending or glazing.

(3) Test No. 3

Temperature 2900°F. (1593°C.) for 5 Hours, Using Distilled Water as Steam Source; Time to Reach Temperature of Hold, 16 Hours

Distilled water was substituted for tap water in order to remove the possibility of having residue salts dislodged and carried along with the steam to react with the specimens. The generator was cleaned with dilute hydrochloric acid and rinsed with distilled water and the test was set up and run essentially the same as test No. 2. The average temperature was 2907°F. and the maximum, 2910°F. The steam generator was operated in the range of 540° to 580°F., and 4250 cc. of distilled water were used. Steam was first introduced at 2700°F. two hours before the holding temperature was reached.

The test pieces had been bleached and were slightly glazed to the same apparent degree as those in test No. 2. The pieces showed no significant change in weight (see Table V) and no bending, and again no bending or glazing of the control bars occurred.

TABLE V

RESULTS OF TEST NO. 3

Brick bars	Weight (gm.) Before	After
Baraboo steamed	32.80	32.83
Eastern steamed	22.88	28.90
Baraboo not steamed	32.51	32.51

The supports used in the control in test No. 2 were used again in the control for test No. 3. After test No. 3, the surfaces of the supports in contact with the porcelain tube were slightly glazed and appeared to be similar to the glazed surface of the control cubes in test No. 1, which were set on high alumina brick (90% alumina). The steamed test specimens showed no glazing where they were in contact with the supports.

Figure 3 shows some of the bars; No. 1 bar is a blank which was not steamed; No. 2 is from Baraboo rock; and No. 3 is from Medina rock; both were subjected to water vapor.

V. Summary

(1) Bars cut from silica brick of normal composition and subjected to the action of water vapor for five hours at 2900°F. (1593°C.) showed no bending or softening but did show a slight surface glaze.

(2) As far as it is safe to draw conclusions from a sixteen-hour laboratory test, water vapor appears to have little or no effect on American silica brick of normal composition at temperatures up to 2900°F.

(3) The results of this investigation do not check those reported by Dodd and indicate that the effects which he observed were due to some cause other than water vapor.

Acknowledgments

The tests described in this paper were carried out under the direction of Clyde L. Thompson and thanks are due him and the laboratory staff, particularly C. Burton Clark.

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MOTTLED OR COLORED SILICA BRICK*

By S. M. Phelps and R. W. Limes†

Abstract

During the burning of silica refractories, spots or areas of dark cream to a reddish-brown color may develop in some of the brick or shapes. This is often called mottling, and its occurrence during the manufacture of the product cannot be definitely controlled. Questions occasionally arise as to whether the colored brick are of as good quality as the uniformly cream-colored brick. No records are available to show or indicate that color as such has been a cause of shorter life or failure in service. Data are presented that were obtained from testing the mottled and light-colored brick, and these show that there is no practical difference between them; consequently, color alone should not be a criterion for judging quality.

The traces of iron present in the silica used are a necessary constituent in the formation of the color. The light-colored product, however, contains the same quantity of iron. It is not entirely clear as to how the iron is present in the two types. Unknown conditions during manufacture are such that the traces of iron may be influenced to form either the light or mottled brick, but the process cannot be controlled.

A considerable amount of experimental work is presented which shows the nature of the color behavior with comments on certain conditions that cause the color formation.

I. Introduction

(1) General

The subject of mottled or colored silica brick has been under discussion for many years, first, because some purchasers of silica refractories are hesitant to accept silica brick which are colored in place of the more usual cream-colored product and, second, because the subject is a curious one from the technological standpoint.

For those who are not familiar with the appearance of mottled silica brick, Fig. 1 shows a color reproduction of several silica shapes that are quite strongly mottled. The color is frequently more pronounced on the surface, but not necessarily so, as can be noted from the broken half brick in the lower left-hand corner of the picture. The range in colors that may develop varies from the normal light cream color of the brick to an increasingly stronger shade of cream, and it may intensify at times to a light reddish brown. It is caused by traces of iron in combination with other constituents and under certain conditions that have not been definitely established. When a kiln of silica brick is opened, there is no assurance that all of the brick will be cream colored; part of them may be mottled. The color occurrence is elusive and is not subject to control during manufacture.

(2) Literature References to Properties

Many references in the literature state that there is no difference in properties between the light and colored silica brick, but there are almost no data to substantiate these claims.

Montgomery and Office[1] pointed out in 1918 that the color in silica brick caused by iron seems to have less effect on the refractoriness than would be expected.

In the following year, Rees[2] stated that the color of silica brick is no criterion of refractoriness.

When investigating the influence of iron on the rate of conversion of quartz in the manufacture of silica brick, Hugill and Rees[3] carried out tests on mottled and normal colored silica brick as manufactured in England. The following data were obtained from samples of both types of brick which were burned in the same kiln:

	Mottled	Normal
True specific gravity	2.425	2.475
Porosity (%)	30.0	30.8
Compressive strength (lb./in.^{2})	3412	3020
Modulus of rupture (lb./in.^{2})	363	229
Ferric oxide (%)	0.96	0.63
Lime (%)	1.52	1.50

In another article, Rees[4] states that mottling has no effect on the behavior or durability in service.

Harman and Badger[5] mention that the flowers or stain of silica brick do not detract from their utility.

Inasmuch as the coloring is the result of the presence of small quantities of iron in the ingredients of the mix,

* The material contained in this paper was presented as "Mottled Silica Brick" by S. M. Phelps and E. C. Petrie at the Forty-First Annual Meeting, The American Ceramic Society, Chicago, Ill., April 18, 1939 (Refractories Division). Received September 20, 1943.

† Senior Industrial Fellow and Industrial Fellow, respectively, Multiple Fellowship of the American Refractories Institute, Mellon Institute, Pittsburgh, Pa.

[1] R. J. Montgomery and L. R. Office, "Notes on Laboratory Testing of Silica Brick," *Jour. Amer. Ceram. Soc.*, **1** [5] 338–52 (1918).

[2] W. J. Rees, "Silica Refractories," *Jour. Birmingham Met. Soc.*, **7**, 151 (1919).

[3] W. Hugill and W. J. Rees, "Influence of Iron Oxide and Iron Sulfides on Rate of Quartz Conversion in Commercial Silica Brick Manufacture," *Trans. Ceram. Soc.* [England], **25** [4] 309–13 (1925–1926); *Ceram. Abs.*, **6** [9] 383 (1927).

[4] W. J. Rees, "Mottled Silica Brick," *Bull. Brit. Refrac. Research Assn.*, No. 30, 1933; reprinted in *Trans. Ceram. Soc.* [England], **35** [6] 284–85 (1936); *Ceram. Abs.*, **16** [1] 23 (1937).

[5] C. G. Harman and A. E. Badger, "Method of Improving Appearance of Silica Brick," *Brick & Clay Record*, **90** [5] 292–94 (1937).

FIG. 1.—The appearance and color of mottling of silica refractories.

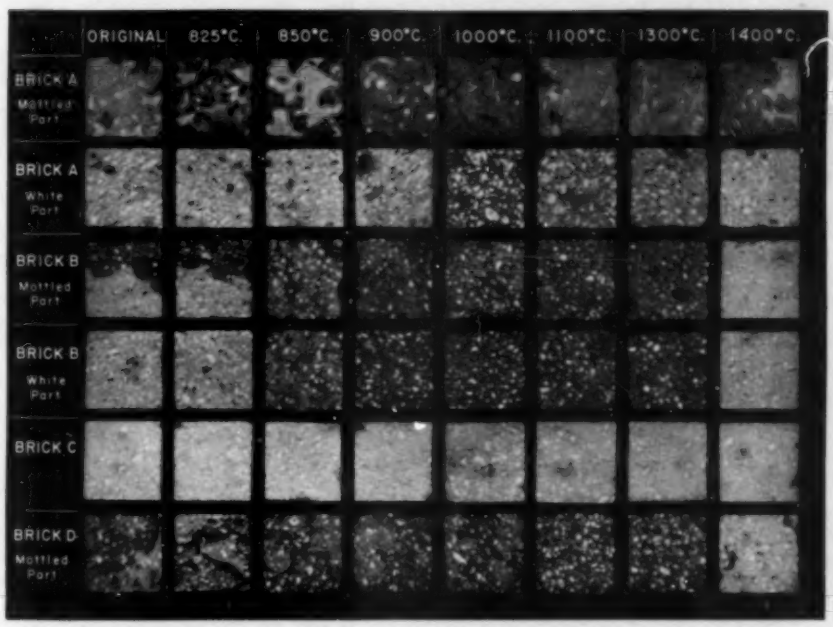

FIG. 3.—The effect of heat treatment at a series of temperatures on several varieties of silica brick.

it might be of interest to point out that many workers claim advantages in the use of iron in substantial quantities to promote the conversion of quartzite to tridymite. The benefits of such have been demonstrated by Hugill and Rees[5] and by Rees.[6] Searle[7] mentions the same subject as does Budnikoff,[8] who claims that the service life of silica brick is doubled when high iron slags are used to bring about conversion.

II. Properties of Light and Colored Brick

In view of the small amount of actual data that have been presented in the literature on the properties of normal and colored silica brick, it was decided to obtain such information on several brands of commercial brick. The data resulting from this part of the study are given in the first portion of the paper, and they should be of particular interest to those involved in the purchase and use of silica refractories. The results of experimental work are given later and show many interesting characteristics of the nature of the coloring. Even though this information may be of more specific interest to the manufacturer or technologist, it should prove interesting to the consumer as a means of learning the nature of this phenomenon.

TABLE I

COMPARATIVE PROPERTIES OF LIGHT-COLORED AND MOTTLED SILICA BRICK

Brick sample	App. specific gravity (avg. 10 brick)	Porosity (avg. 10 brick, %)	Modulus of rupture (avg. 15 brick, lb./in.²)	Load test, 50 lb./in.² at 1625°C. (2960°F.) (avg. 2 brick, %)
		Brand A		
Light-colored	2.33	25.3	690	+0.75
Mottled	2.33	25.1	720	+0.8
		Brand E		
Light-colored	2.30	28.7	585	−0.2
Mottled	2.31	28.6	565	−0.15
		Brand F		
Light-colored	2.29	28.1	1230	−0.15
Mottled	2.30	31.7	720	−0.2

(1) Samples

An attempt to secure samples of both the normal and colored products made under exactly the same conditions was not practical because the occurrence of the mottling is highly unpredictable and, as might be expected, does not develop when an effort is made to produce it. Samples were therefore selected from brick in storage at several plants. These brick were strongly colored and, for comparative purposes, samples of the normal colored product were included. In various phases of the study, seven brands of brick were used, taken from plants in five widely distributed districts of the country.

(2) Tests Used and Data Obtained

In obtaining the comparative properties of the two types of brick, the available tests for evaluating silica refractories were used. These tests were carried out on the light and colored brick of the three brands, A, E, and F, and the data obtained are presented in Table I. Brief comments concerning these properties are as follows:

(*A*) *Apparent Specific Gravity:* Samples weighing approximately 200 gm. were taken from ten normal and colored brick to obtain a satisfactory average. The results show that the usual changes brought about during the burning are virtually the same in the light and mottled samples from each brand.

(*B*) *Porosity:* The apparent specific gravity samples were used for determining porosity. The data show almost no difference except in brand F where the mottled brick were 3.6% higher than those of the normal color, which indicates that the mix for these brick was not well packed during molding.

(*C*) *Modulus of Rupture:* Fifteen brick in both conditions of color were taken from each brand to determine the modulus of rupture. In brand A, the mottled brick were slightly higher in strength, whereas a lower value was obtained for brand E. The normal-colored product in brand F, however, showed an abnormally high strength, and although the companion brick in the colored condition had lower strength, the value was in the range of high strength for silica brick.

(*D*) *Behavior Under Load at High Temperatures:* The procedure for the hot-load test is rather severe, making use of 50 lb. per sq. in. load and a temperature of 1625°C. (2960°F.) for a period of ½ hour. The average results of two brick of each type are given, and none of the brick showed any indications of failure under these severe conditions. The behavior of each material, moreover, was normal.

(*E*) *Thermal Expansion:* It was thought advisable to obtain the thermal expansion of the two varieties to learn whether any significant difference was present. The test specimen used measured 1 in. square in cross section and 8 in. long. By careful selection, it was possible to obtain from brand A a brick from which a specimen could be cut in which the color throughout was almost a uniform red-brown. The data obtained from this sample and from a companion specimen taken from a light-colored brick are presented in Fig. 2. This information shows that there is no significant difference between the materials in the two conditions of color. The permanent expansion in this test resulting from the heat-treatment was 0.09% for the light sample and 0.10% for the dark one. Additional information on thermal expansion is given later in section III (5).

(*F*) *Abrasion Test:* In addition to the foregoing tests to determine the physical properties of the two types of brick, a sandblast was used to abrade samples that showed distinct areas of mottling in order to learn whether any difference in hardness or toughness

[6] W. J. Rees, "Further Note on Influence of Iron Oxide in Promoting Inversion of Silica," *Trans. Ceram. Soc.* [England], **25** [4] 314–17 (1925–1926); *Ceram. Abs.*, **6** [9] 383 (1927).

[7] A. B. Searle, Encyclopedia of the Ceramic Industries, Vol. III, p. 143. E. Benn, Ltd., London, 1930; *Ceram. Abs.*, **10** [5] 397 (1931).

[8] P. P. Budnikoff, "Silica Refractories That Give Double Service," *Ceram. Age*, **22** [5] 130–31 (1933); *Ceram. Abs.*, **13** [7] 184 (1934).

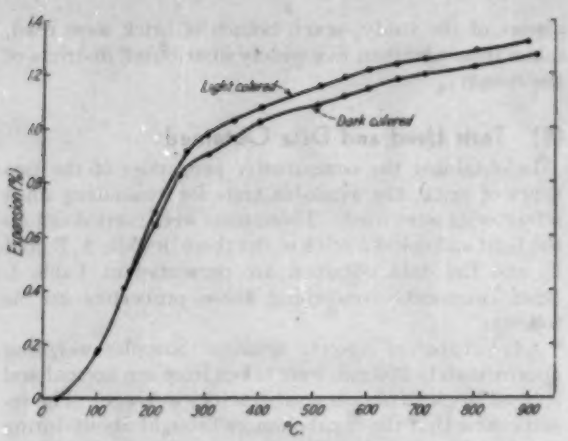

FIG. 2.—Thermal expansion data obtained by testing the cream- and dark-colored portions of sample A.

occurred as a result of color development. Tests conducted on five brick and three shapes showed that during the abrading of approximately 1/4 in. of the surface of the samples there was no discernible difference in the amount of material removed from the light or dark areas.

(*G*) *Chemical Composition:* The chemical composition of the brick used in this portion of the study was not obtained, but Table IV shows the composition of four brands used in the other portion of the study. That information shows, among other things, that there is nothing abnormal about the composition of the mottled versus white portions of the brick.

(3) Conclusions on Properties of Light and Colored Silica Brick

The three brands of commercial brick studied show that the mottled or colored samples have properties comparable with those of the cream-colored brick. The quality of silica refractories should be judged by their physical properties, for example, strength, specific gravity, and behavior in a suitable hot load test. An inexcusable waste and economic loss may occur when silica brick are appraised only on the basis of color.

III. Nature and Cause of Coloring

(1) Effect of Heat-Treatment on Color

It is a well-known fact that mottled brick can be changed to a uniform cream color by heat-treatment at high temperatures. No information apparently is available in the literature concerning the effects of temperature, duration of heating, or the rate of cooling in bringing about the color change; suitable heat-treatment studies were therefore conducted on samples of light as well as colored brick.

Small test pieces measuring 1 1/2 by 1 1/2 by 3/4 in. were cut from the silica brick or shapes by a thin abrasive cut-off wheel. An electrically heated muffle furnace of the Globar type was used and the samples were subjected to a series of heating tests at temperatures ranging from 825°C. (1515°F.) to 1400°C. (2550°F.).

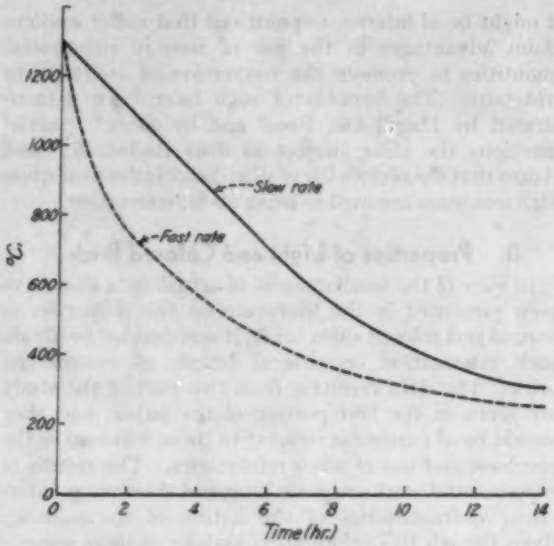

FIG. 4.—Rates of cooling used in heat-treatment tests of silica brick.

The temperature was maintained for a three-hour period, and the rate at which the samples were allowed to cool in the furnace was 100°C. (180°F.) per hour until 650°C. (1200°F.) was reached, after which the rate was slower because of the natural cooling characteristics of the furnace itself. This rate of cooling will be referred to hereafter as the "slow" and is plotted in Fig. 4 with the normal rate of cooling of the furnace, which will be referred to later as the "fast."

The appearance of the heated pieces is presented in Fig. 3. A brief description of the samples used (A, B, C, and D), together with their behavior, is as follows:

Specimens were cut from the light and mottled portions of brick from brands A and B. The properties of brand A have been described earlier in the paper. Brand B was used because of its susceptibility to color change by heat-treatment. Brick C was selected because of its unusual whiteness. Sample D was the most intensely colored brand of brick obtained for the study. The chemical compositions of samples B, C, and D are presented in Table IV.

The heat-treatment at the respective temperatures produced interesting changes in the color of all the samples. The color plate reproduces the progressive changes as well as can be expected, but the following comments are made as a result of examining the actual samples:

The test pieces taken from the mottled part of sample A began to darken at 825°C. (1515°F.) and progressed to maximum depth of color at 1000°C. (1830°F.), after which the color lightened until 1400°C. (2550°F.) was reached, which for some unaccountable reason caused an irregular behavior of mottling to take place.

The specimens taken from the white portion of brick A did not begin to show darkening of color until 900°C. (1650°F.) was reached, but they became quite dark at 1000°C. (1830°F.), which appears to be the critical temperature for those samples. As the temperature

increased, the color lightened so that at 1400°C. (2550°F.) the color had returned to its original tint.

In brand B, both the light and mottled specimens showed pronounced darkening at 850°C. (1560°F.) and remained dark until the 1400°C. (2550°F.) treatment. The temperature at which the color developed in the case of this sample is an interesting feature because no discernible change had taken place at 825°C. (1515°F.); nevertheless, pronounced darkening developed during the next 50°C. (90°F.).

An important feature of the behavior of silica brick is brought out in samples A and B. The fact is demonstrated here that the lighter colored portions of a mottled brick can be darkened by suitable heating. The constituents required to cause the color are present in the light-colored areas, and it is only necessary to provide suitable heat-treatment to cause these ingredients to rearrange themselves to produce the color.

Brick C is less amenable to color change by heat-treatment, and examination of the heated samples themselves shows that at 1000°C. (1830°F.) the brick darkens slightly. As will be shown later, time is an important factor in causing this sample to develop color.

Brand D showed in its original condition variegated colors, ranging from buff through greenish yellow to red-brown. Because of the extent of coloring in the brick themselves, it was not possible to prepare samples which were of uniform light color. The heat-treatment has caused this sample to darken to its maximum shade at 850°C. (1560°F.) and to remain in that condition until the 1400°C. (2550°F.) test, in which it made the pronounced change of turning to the typical light cream color of silica brick.

In addition to these tests, pieces taken from the light portion of brand B were heated to 900°C. (1650°F.) so as to produce the dark color. They were then heated to 1600°C. (2910°F.) and held at that temperature for five hours, which caused a very white color to develop. These pieces subsequently were heated again to 900°C. (1650°F.), which in turn caused the brown color to reappear although it was not quite so deep as that produced by the first 900°C. (1650°F.) heating. It is surprising that the high-temperature treatment did not cause the color-forming and other constituents of the brick to combine in a manner that would prevent the reoccurrence of the color compounds when the sample was heated a second time at the lower temperature.

It may be of interest to point out that in the semi-precious stone industry the practice[9] of heating crystalline quartz at critical temperatures to produce the yellow of citrine quartz and the dark brown color of Spanish topaz is widely used.

(2) Effect of Time During Treatment at 900°C. (1650°F.)

This series of trials was carried out to gain an idea of the influence of time on the color development when heated in the critical temperature range. The brands of brick used were the same as those employed in the previous series where the effect of temperature of heat treatment was investigated. The heat-treatment was conducted at 900°C. (1650°F.) for periods of 1 hour and 45 hours. The samples were allowed to cool in the furnace at the "slow" rate shown in Fig. 4.

The color effects obtained are portrayed in Fig. 5, where it can be observed that the longer period of time caused a darker hue to be developed in the test pieces taken from each type of brick. It is well to note the behavior of the samples from brick A and particularly those from C. In the temperature series of tests described, the white portion of sample A did not darken to a strong shade, even at its critical temperature of 1000°C. (1830°F.). The prolonged heating of 45 hours, however, caused the color to deepen considerably and to the extent of what appears to be the ultimate depth of color that may develop in any of these samples. The resistant sample C was likewise affected to a marked degree by the extended period of heating. These tests and those previously described make it appear that almost any silica brick could be darkened in color provided heating for a sufficient period of time and at a suitable temperature was used.

(3) Rate of Cooling Heated Samples

During the early part of the work on heat-treatment of samples, observations were made on the important effect of the rate at which the heated specimens were cooled. For example, pieces of brick B were heated to 1200°C. (2190°F.), some of which were taken from the furnace and were cooled by an air blast and others were buried in powdered insulating material. A third group was allowed to cool in the furnace at the "slow" rate (Fig. 4). The pieces cooled by air blast were white when cold, but both of the other sets were a reddish-brown color. In view of this behavior, samples of the mottled portion of brand B were heated in separate tests at intervals of 100°C. (180°F.) from 900°C. (1650°F.) to 1400°C (2550°F.), and after heating they were cooled at the "fast" and the "slow" rates as given in Fig. 4. The results of this series of trials are presented in Fig. 6, where a bleaching effect is noted in the case of the faster rate of cooling from the temperatures above 1000°C. (1830°F.), and this effect becomes more noticeable as the temperature increases. It would appear from this result that rapid cooling within certain temperature ranges may cause compounds or glasses to solidify or "freeze" in a manner that prevents the formation of color.

Heating and cooling trials were made to show this feature more clearly. Samples from the mottled portion of brick B were heated at 1300°C. (2370°F.), which would cause the dark color to form provided they were cooled slowly. The furnace temperature, however, was reduced at the "slow" rate to 1000°C. (1830°F.), at which time some of the test pieces were removed and allowed to cool by exposure in the atmosphere. A similar procedure was used in cooling the furnace to 900°C. (1650°F.) and to 800°C. (1470°F.), together with the removal of the samples for cooling in the atmosphere.

[9] H. C. Dake, Frank L. Fleener, and Ben Hur Wilson, Quartz Family Minerals, p. 175. Whittlesey House, McGraw-Hill Book Co., New York, 1938. 304 pp.; *Ceram. Abs.*, **18** [9] 354 (1939).

A complementary procedure was used to show the effects of a faster rate of cooling from 1300°C. (2370°F.) to the three temperatures, followed by "slow" cooling from each of the lower temperatures. The method used was to draw the specimens from the furnace operating at 1300°C. (2370°F.) and place them in a second furnace which had been heated to 1000°C. (1830°F.), after which the furnace and the test pieces were cooled at the "slow" rate. In other runs, the second furnace was heated to 900°C. (1650°F.) and 800°C. (1470°F.) with subsequent "slow" cooling. The results of the two series of tests are described in Table II.

The behavior of the samples shows that when the "slow" rate of cooling is used, which allows the color to develop, the actual color formation is effected at temperatures below 1000°C. (1830°F.). The tests using the fast rate of cooling from 1300°C. (2370°F.) show that the color-forming temperature is 800°C. (1470°F.) or above. This would make it seem that the critical temperature for sample B would occur in the vicinity of 900°C. (1650°F.). Allowance must be made, however, for the method used, because when the samples were placed in the furnace at the lower temperature their rate of cooling to that temperature would not be as rapid as could be desired. The outstanding feature of this work is that when the sample was cooled from 1300°C. (2370°F.) to 800°C. (1470°F.), it was a reddish-brown color or a light buff, depending on the manner in which the temperature was reduced.

The information obtained from the rate-of-cooling trials may help to explain why brick in the center of a kiln are more likely to develop color than those forming the outside and top of the setting. The brick in the latter position are more likely to be cooled at a fast rate to a temperature that is below the critical range, and for this reason, they would not develop color. Perhaps a revision of the practice of cooling kilns would be worth while; for example, after cooling by the normal method had progressed sufficiently, the center might be cooled by forcing air into the kiln through the chimney flue. Cycles of cooling by the two methods might also be considered.

(4) Effect of Sulfur and Gas Atmospheres on Mottling

The suggestion has been made from time to time that sulfur might be an important factor in causing color formation. Phelps[10] pointed out that the treatment of silica brick at 950°C. (1740°F.) for a period of 72 hours in an atmosphere of sulfur dioxide caused light-colored brick to change to the color of the mottled variety. It is realized now that this coloring may have been caused by the heat-treatment rather than by the presence of sulfur dioxide. During the drying of silica brick, some of the lime would be converted to calcium sulfate, provided waste heat from the kilns were circulated through the drier. Furthermore, as

TABLE II

EFFECT OF RATES OF COOLING ON MOTTLED PORTIONS OF BRICK B

Lower temp. to which samples were cooled at two rates from 1300°C. (2370°F.)	Color appearance resulting from different methods of cooling	
	Cooled slowly from 1300°C. (2370°F.) to lower temp.; then rapidly until cold	Cooled fast from 1300°C. (2370°F.) to lower temp.; then slowly until cold
1000°C. (1830°F.)	Light buff throughout	Reddish brown (same as slow cooling)
900°C. (1650°F.)	Dark buff toward red	Dark but indications of color removal
800°C. (1470°F.)	Reddish brown (same as slow cooling)	Light buff throughout

Mellor[11] points out, dilute sulfuric acid may be formed on the brick during the early stages of burning by reason of the condensation of moisture and sulfur oxides which would be present in the kiln gases coming from the burning coal. He states that "the sulphates of lime and iron which are formed are decomposed only at relatively high temperatures. There is not then time for the liberated lime and ferric oxide to associate together to form the pale-colored ferrite." Rees[4] expresses a similar viewpoint. In the opinion of the present authors, there is some question as to whether sulfur as such has any influence in the actual color formation. The solubility of the sulfates formed may, however, enter the picture. This subject will be discussed later.

It would be well to relate the experience of a manufacturer of silica brick who converted his kilns from coal to gas firing. During the course of a two-year period of firing with gas, a high percentage of the ware was a strong red-brown color. In endeavoring to learn the cause of the color, the possibility of sufur was considered, and it was found that the total amount of sulfur from the combustion of the gas was less than $^1/_{100}$ of that which might be expected by burning coal. It was also learned, incidentally, that a low draft was used and a slightly reducing atmosphere was maintained. The strongly colored brick from this plant, however, were of good quality and high in mechanical strength.

In connection with the effect of gas atmosphere on color changes, the results of the first experimental trial may be of interest. Silica-brick samples were heated to 1200°C. (2190°F.) in the electric furnace, the muffle of which was made of silicon carbide. The samples darkened to such an extent that it was believed at the time that a reducing atmosphere might exist within the muffle. This test was repeated, however, using a fused alumina muffle; identical results were obtained. The silicon carbide muffle was used in subsequent work because of its better thermal conductivity.

[10] S. M. Phelps, "Studies of Effect of Chlorine, Sulfur Dioxide, and Carbon Monoxide on Various Refractories," *Amer. Refrac. Inst. Bull.*, No. 9, 8 pp. (1927); *Ceram. Abs.*, **6** [11] 524 (1927).

[11] J. W. Mellor, "Discoloration of Refractories by 'Iron,'" *Trans. Ceram. Soc.* [England], **32** [9] 403–14 (1932–1933); reprinted in *Bull. Brit. Refrac. Research Assn.*, No. 31, June, 1933; *Ceram. Abs.*, **13** [3] 62 (1934).

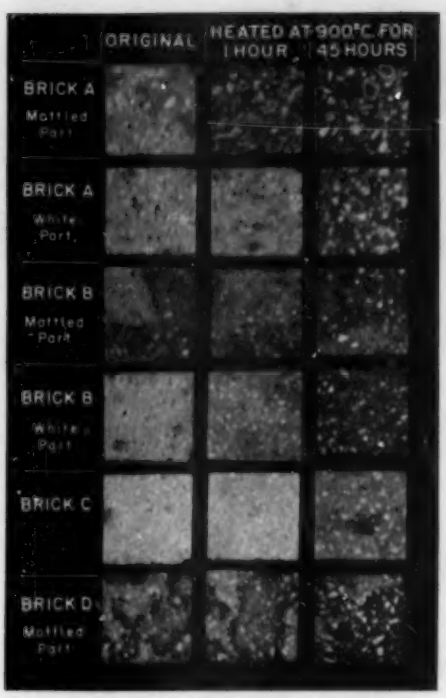

FIG. 5.—The effect of time during heat treatment at 900°C. (1650°F.).

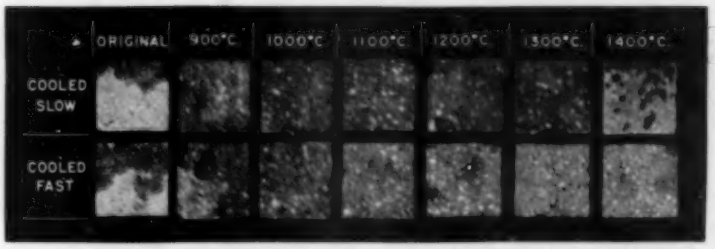

FIG. 6.—Color changes caused by slow and rapid cooling from various temperatures.

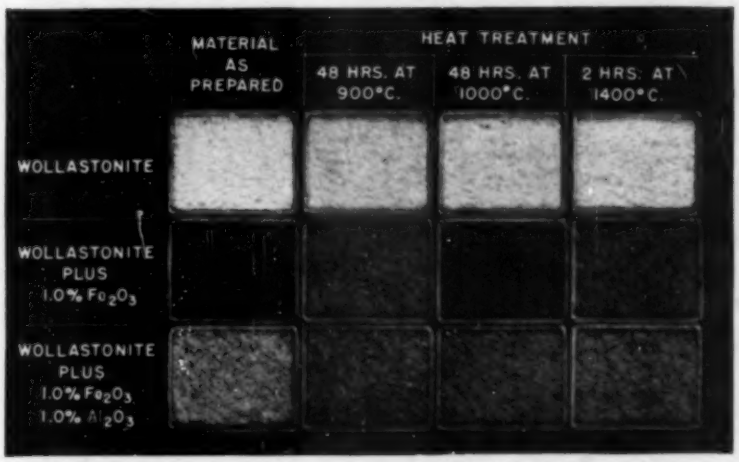

FIG. 8.—Prepared wollastonite and wollastonite with additions of iron and iron plus alumina which have been heated to various temperatures.

As a matter of interest, trials were made to learn whether rapid cooling in atmospheres of sulfur dioxide, carbon dioxide, or steam would give effects different from air. Samples of the mottled portion of brick B were heated to 1300°C. (2370°F.) and were then placed in a suitable container through which a blast of a gas or steam was forced. Each of the cooled specimens had much the same appearance as those cooled by air except that these were a slightly gray-cream color.

It was thought worth while to heat and cool slowly suitable samples while they were exposed to atmospheres of sulfur dioxide and carbon dioxide. A $2^1/_2$-in. (inside diameter) closed-end refractory tube was used to accommodate $1^1/_2$- by $1^1/_2$- by $^3/_4$-in. samples. The refractory tubes for gas delivery and exhaust, as well as a thermocouple protection tube, were sealed in the open end of the container. The samples were the light portion of brick B, the uniformly light-colored brand C, and the colored portion of lot E, data on which have been given in section II and Table I. The heat-treatment when using each of the gases was the same, holding a temperature of 1300°C. (2370°F.) for three hours, followed by "slow" cooling. An appreciable flow of the gas was maintained from the beginning and until the samples were cooled. A description of the appearance of the tested pieces is as follows:

Sample	In SO_2 treatment	In CO_2 treatment
B (light portion)	Reddish brown*	Mottled cream
C (cream)	Cream	Cream
E (mottled)	Reddish brown*	Dull red

* Samples not so dark in color as similar samples cooled in air.

From the foregoing experiment, sulfur dioxide does not seem to be any more effective than an atmosphere of air in causing the color formation, and carbon dioxide may be found to have a retarding influence.

Such tests do not prove that sulfur dioxide is a factor in the color formation during the actual firing of the brick, but by summarizing all of the available information and considering the fact that ordinary light-colored brick can be converted to a colored product by heat-treatment alone, it may be surmised that sulfur dioxide as such is not a factor of any consequence.

(5) Color as Affecting Thermal Expansion

Although thermal expansion data for both light and colored samples of brick have been presented in section II (2) *E* and Fig. 2, it may be of interest to record more conclusive work which would distinguish any difference caused by the color-forming constituents.

Test pieces measuring 1 in. square in cross section and 8 in. long were cut from adjacent areas in a cream-colored brick of brand B. One of these was used for a thermal expansion test, and the second sample was heated to 900°C. (1650°F.) for five hours and was slowly cooled, which produced a dark red color. The thermal expansion of this sample was also determined, and the data for both test pieces are presented in Fig. 7. It will be noted that in considering the probable error of such a test, the difference in behavior of the two samples has no significance.

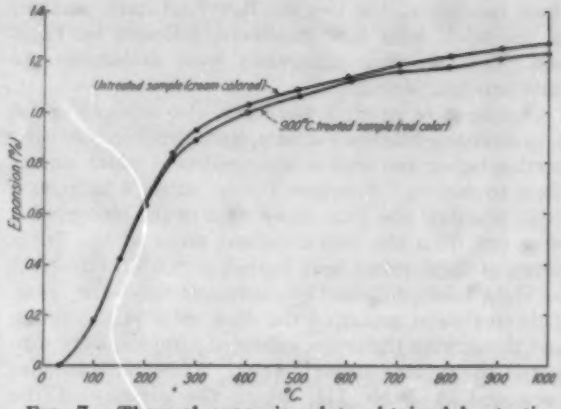

FIG. 7.—Thermal expansion data obtained by testing samples taken from the light portion of a brick from brand B, one of which had been changed to a red color by heat-treatment.

(6) Crushing Strength of Brand B in Both Conditions of Color

The strength of light and colored brick was obtained as modulus of rupture and has been presented in section II (2) *C*. Additional strength tests were carried out, obtaining the crushing strength of samples from brick B, which had been prepared in various ways by heat-treatment.

In one set of tests, ten $^3/_4$-in. cubes were cut from the cream and from the colored portions of the brick, and all of these were heated at 1200°C. (2190°F.) for three hours. Five of the light and five of the dark-colored cubes were drawn from the heated furnace and were cooled rapidly. The remaining five of each kind were allowed to cool in the furnace at the "slow" rate. This method resulted in five light-colored and five dark cubes from the group of ten cubes taken originally from each area of the brick.

Crushing-strength tests were carried out on the four sets of cubes, and these data are presented in Table III. It is realized that the limited size of the test specimens which could be cut from these brick (mottled areas) makes their dimensions smaller than would be desired for crushing strength determinations; these data may therefore be considered as only indicative of the effect of color change on strength. Under

TABLE III

CRUSHING STRENGTH DATA OBTAINED FROM VARIOUS SAMPLES OF SILICA BRICK B

Sample description and heat-treatment	Cooling treatment and color change	Crushing strength (lb./in.^{2})
Cubes cut from cream portion, heat-treated at 1200°C. (2190°F.)	"Slow," turned brown	5145
	Fast, remained cream	5955
Cubes cut from brown portion, heat-treated at 1200°C. (2190°F.)	"Slow," remained brown	5955
	Fast, turned cream	5660
(Values average of 5 tests on $^3/_4$-in. cubes)		
Cubes cut from cream portion of brick		6125
Similar cubes after 8 hr. heating at 900°C. (1650°F.)	"Slow," turned dark brown	5485

these conditions, the original light and dark portions of the brick after heat-treatment, followed by rapid and "slow" cooling, apparently have essentially the same crushing strengths.

Comparative strength tests were also made on brand B to show the difference in samples taken from the light portion before and after a heat-treatment which caused them to darken. Fourteen $1^1/_4$-in. cubes, which are a more practical size than those used in the former test, were cut from the cream-colored areas of the brick. Seven of these cubes were heated at 900°C. (1650°F.) for eight hours, followed by cooling at the "slow" rate. This treatment produced the dark color in the cubes, and these, with the seven unheated samples, were subjected to crushing-strength tests. These data are also presented in Table III, where the samples of the original brick are shown to be approximately 10% stronger than similar test pieces which had been changed to a brown color. In view of the fact that the darker samples had been heated as well as the lack of perfect reproducibility of the test data, this order of difference in strength may not be too significant.

(7) Chemical Composition as Related to Color Formation

Small quantities of iron in silica brick are responsible for the color formation, but the amount present is not necessarily an index to the intensity or extent of coloring which can be developed. Many factors must be considered in this connection, such as the percentage of lime, alumina, and possibly the magnesia and alkalis in the product. Furthermore, the ratio in which the iron, alumina, and lime are present is important. Small quantities of iron and alumina are always part of the composition of quartzites used for the manufacture of silica brick, but the way in which they may be present, that is, their distribution and particle size, may be factors of consequence. There is evidence that, with a given amount of iron, the lime and alumina can be adjusted to produce the composition that would develop a minimum of color under the adverse conditions that would cause color formation. Golla,[12] for example, reports that a dark color was produced when the normal lime content of brick was raised by 1% and that the addition of small amounts of clay (0.5% in most cases) to the standard mix eliminated the brown spots almost completely.

Manufacturers of silica brick, in cooperation with producers of lime, have found that the way in which the lime is made as well as its composition (including magnesia) may have a bearing on the extent of mottling in the final product.

Another feature which should be mentioned is the possibility that the lack of uniformity of chemical composition in areas of a brick may cause mottling. It is customary for mottling to develop as circular areas of color, which immediately suggests that a liquid has been involved and that it has caused a change in the composition of that area to one more favorable to the color formation. There are several possible ways in which small differences in the composition of areas of the brick may develop, especially because only a small variation would be responsible for the color formation. Golla[12] found that a wet mix sometimes will give more red spots than a dry one, and he explains this effect by the fact that the wet mix will allow the milk of lime to work toward the surface of the brick. This action would help to explain why the side of a brick which was on the pallet during drying is often less mottled than the other surfaces. As has been explained in section III (4), the formation of calcium sulfate may take place during drying or the early stages of firing. The sulfate is more soluble than the hydroxide, which could account for its migration to the surface or its accumulation in areas of the brick. The solubility of calcium sulfate might make it seem that such a process would be quite effective in transposing the calcium content, but when the moisture available and the amount of calcium in the sulfate are considered, the process is not particularly effective.

The behavior of small differences in composition of a brick is displayed in the color plate of Fig. 1, where a white streak appears on the bottom brick at the left side and along the front vertical edge of the shape on the right side. These white areas in the otherwise mottled sections were caused by the silica sand used during setting of the brick in the kiln. The fine particles of silica altered the composition of the otherwise color-forming compound on the surface of the brick during firing. These streaks demonstrate the fact that changes in composition take place during burning. It is not unreasonable therefore to expect that glass would be formed in accumulations or around particles of fluxing constituents during stages of the firing and that these would be sufficiently liquid to allow them to spread over relatively large areas.

The small quantity of the actual color compound and the way in which it is distributed between the particles of silica minerals in the brick make it impracticable to obtain a sample of the colored material for chemical analysis or even for a satisfactory petrographic examination. It is necessary, therefore, to resort to the selection of samples from the light and cream-colored areas for chemical analysis. Data obtained from such samples are of interest, however, because they show any difference in the average composition of the areas in the order of 0.1% or less of the constituents.

Table IV presents the chemical composition* of both the light and colored areas of brand B, which has been used throughout this study, and similar data for brand G, which also showed pronounced mottling. The analysis of a sample of the dark portion of the most highly colored brick of the study, brand D, is also given as well as the data for the outstanding light-colored brick of the entire group of samples, brand C.

[12] Hans Golla, "Red-Spotted Silica Brick," *Tonind.-Ztg.*, **55** [93] 1285–87 (1931); *Ceram. Abs.*, **11** [5] 311 (1932).

* Chemical analyses reported in this paper were conducted by E. B. Read, Industrial Fellow on the Multiple Fellowship of the American Refractories Institute, Mellon Institute, Pittsburgh, Pa.

TABLE IV

CHEMICAL COMPOSITION (%) OF FOUR BRANDS OF SILICA BRICK USED

Constituent	Brick B		Brick G		Brick D	Brick C
	White part	Mottled part	White part	Mottled part	Mottled part	White brick
Silica	96.29	96.32	96.40	96.34	96.49	95.70
Alumina	0.50	0.52	0.41	0.42	0.31	1.19
Ferric oxide	0.59	0.59	0.46	0.48	0.74	0.40
Titania	0.10	0.10	0.04	0.04	0.05	0.12
Lime	2.04	2.07	2.59	2.56	2.01	2.05
Magnesia	0.06	0.05	0.04	0.05	0.05	0.16
Alkalis	0.18	0.18	0.07	0.07	0.27	0.08
Total	99.76	99.83	100.01	99.96	99.92	99.70

A surprising feature of the composition of brands B and G is the presence of an almost identical percentage of each constituent in the samples of the light and colored product. This information helps to explain why the light-colored areas can be converted to the dark product by suitable heat-treatment and, conversely, why the mottling can be changed to the cream color.

It is well known in the silica brick industry that high iron and low alumina generally cause a dark-colored product and that a light color results when the ratio of these constituents is reversed. This fact is brought out in comparing the composition of the dark-colored brand D and the uniformly cream-colored brand C which, for all practical purposes, have the same composition except for the percentages of iron and alumina. These data, moreover, show the order of the differences in the quantity of these constituents, which are responsible for the pronounced differences in color displayed by these brands.

Curiosity prompted experimental work which would indicate the amount of iron and lime that could be extracted from silica brick by treatment with dilute hydrochloric acid, especially because calcium silicate (wollastonite) is soluble in hydrochloric acid. Samples of the cream and colored portions of brand B and of the light-colored brick C were ground to pass a 100-mesh sieve and were treated with 1 to 1 hydrochloric acid at 88°C. (190°F.) for five hours. After filtering, the iron and lime contents were determined on the filtrates. The results of this work are given in Table V. Virtually the same percentage of each constituent was extracted from the cream and colored portions of brick B, which is another indication that the two portions of this brick possess similar characteristics. An interesting feature is that the light-colored product, C, is of such nature that a relatively small amount of these constituents was extracted by the acid-treatment. Brands B and C contain practically the same amount of lime, and B contains only 0.19% more iron than C. The speculation may be made that the difference in the amounts of iron and lime extracted could be accounted for by the higher alumina content of the light-colored brick C.

The residues from the acid extraction of the cream and colored samples of brick B (100-mesh) were heated at 900°C. (1650°F.) for three hours, together with similar samples which had not been acid-treated.

TABLE V

EXTRACTION OF IRON AND LIME BY HYDROCHLORIC ACID

Sample	Constituent	Amount present (%)	Amount extracted by acid (%)	% of total extracted by acid
Brick B, cream portion	Fe_2O_3	0.59	0.36	61.0
	CaO	2.04	1.62	79.5
Brick B, colored portion	Fe_2O_3	0.59	0.36	61.0
	CaO	2.07	1.63	78.7
Brick C, cream-brick	Fe_2O_3	0.40	0.08	20.0
	CaO	2.05	0.38	18.5

Both of the leached samples showed a cream color after the heating, and the unleached samples darkened to the same red-brown shade. Acid-treatment on pieces of brick, however, does not seem to be effective because samples of the light and dark portions of brick B were treated with 1 to 1 hydrochloric acid for 48 hours and were then thoroughly washed with distilled water. On heating these samples at 900°C. (1650°F.) for three hours, followed by "slow" cooling, both samples changed to a red-brown.

(8) Microscopic Examination of Brick

As has been stated previously, the extremely small quantity of the color-forming material in the brick and the way in which it is present make its study rather difficult. Microscopic examination, however, reveals the nature of the color-forming material and indicates the process which takes place in its formation.

Samples F and A in the light and colored conditions, as well as heat-treated samples of B, were examined by Fettke,* and excerpts from his report of December, 1938, are presented in paragraphs (A) to (D), inclusive.

(*A*) *Brick Sample F:* Thin sections were prepared from widely separated areas of the brick so as to represent the light and colored portions. Examination of the light-colored material showed the matrix to be a light cream color. There were no crystalline silicates between the tridymite crystals, and only a small amount of glass was present. In the case of the sample representing the colored region, extensive portions of the matrix were a yellowish-brown color. Aggregates of fibrous crystalline silicate were observed, the largest individual fibers being 0.0025 by 0.04 mm. These fibers were identified tentatively as beta-wollastonite. Interference colors of the first to second order indicate the birefringence to be that of wollastonite. Most of the fibers appeared to possess parallel extinction, but some apparently give oblique extinction. The aggregates were so minute that it was impossible to isolate any for accurate determination of the indices of refraction, but their indices appeared to fall within the range of wollastonite. The aggregate possessed a pale yellow color in transmitted light, which may be due to the presence of some iron silicate in solid solution.

(*B*) *Brick Sample A:* Examination of the light-colored sample showed that the matrix consisted

* C. R. Fettke, Professor of Geology, Carnegie Institute of Technology, Pittsburgh, Pa.

largely of well-developed tridymite crystals and that no crystalline silicates were present. A pale yellow crystalline silicate in the form of minute aggregates between the tridymite crystals of the matrix was observed in the colored sample. Individual units had dimensions up to 0.0075 by 0.018 mm. Their optical properties were similar to those observed in the crystalline silicate in the mottled portion of sample F. Unlike sample F, however, the crystalline silicate in brand A contained minute dendritic inclusions of a deep reddish-brown substance with relatively high index of refraction.

(*C*) *Heat-Treated Samples B:* Examination was carried out on samples taken from the light-colored portion of brick B and similar samples after having been heat-treated to a series of temperatures from 800°C. (1470°F.) to 1000°C. (1830°F.). The heat-treatment caused coloring to begin to develop at 800°C. (1470°F.) and progressed until the samples were dark in color at the higher temperature.

Examination of the unheated sample showed the matrix to contain well-developed tridymite crystals between which some glass and a crystalline silicate were present. The crystalline silicate was a pale yellow color with optical properties similar to those observed in sample F. The 800°C. (1470°F.) sample showed a somewhat deeper pale yellowish-brown color, whereas a richer brown had developed in the 875°C. (1605°F.) sample. The samples heated to 950°C. (1740°F.) and 1000°C. (1830°F.) showed minute needlelike inclusions of a deep reddish-brown substance in the crystalline silicate. These had separated apparently from the silicate, which possessed a paler yellowish-brown color than that exhibited by the silicate in the sample heated to 875°C. (1605°F.). The needles represented some iron compound, possibly hematite, which had separated from solid solution in the silicate.

(*D*) *Conclusions:* The mottling exhibited by the samples is associated with the development of a crystalline compound from the glass of the matrix. This compound has been identified tentatively as wollastonite with some iron silicate in solid solution, which gives it a pale yellow to yellowish-brown color. The depth of color is probably influenced by the state of oxidation of the iron. The crystalline compound unfortunately occurs in such minute aggregates that it was not possible to be positive of its identity. Where the compound occurred in the matrix, the space it occupied was somewhat greater than where the glass phase was present, which suggests the possibility that a slightly higher lime content occurred in the colored portions of the brick.

Memnonova[13] has reported on the microscopic examination of spotted silica brick, and he believes that the color is caused by the presence of pseudowollastonite and calcium ferrite. This report also points out that a higher lime content may be present in the color-forming areas.

Birch[14] has suggested recently that the actual color-forming constituent may be the black mineral, hedenbergite ($CaO \cdot FeO \cdot 2SiO_2$). Equilibrium diagrams show that ferrous oxide may be held in solid solution by the wollastonite but unmixing takes place with suitable heat-treatment (800° to 1000°C.) (1470° to 1830°F.), resulting in the formation of hedenbergite.

Microscopic examinations may be summarized as showing that the color development progresses through the formation of wollastonite from the glass in the matrix of the brick. This crystalline material is colored by the presence of iron, and as the depth of color increases by suitable heat-treatment, the iron forms a more intensely colored product. The end product may be hematite, calcium ferrite, or, more conceivably, hedenbergite as suggested. It has been demonstrated earlier in this paper that whatever process of color formation is involved, the reverse action can be brought about by heat-treatment, which means that the iron is taken back into solid solution and forms a lighter colored material.

(9) Experimental Synthetic Color-Forming Compounds

Additional experimental work has been carried out recently for this paper on the preparation of synthetic compounds which might throw more light on the composition of the actual color-forming materials. Sufficient time was not available to permit the work to amount to more than an indication of what might be accomplished by extending the series of trials and by using a more thorough technique.

Small quantities were made of wollastonite, wollastonite plus 1.0% of ferric oxide, and wollastonite plus 1.0% of ferric oxide plus 1.0% of alumina. The prepared materials were heat-treated at 900°C. (1650°F.), 1000°C. (1830°F.), and 1400°C. (2550°F.) to learn of color changes which might occur and whether these changes would be related to or would parallel the behavior of mottling in silica refractories.

The lime was prepared from calcium carbonate which analyzed 99.8% of $CaCO_3$ and contained 0.003% of Fe. The silica was obtained by dehydrating rather pure silicic acid which contained 0.10% of nonvolatile material in hydrofluoric acid and which had an Fe content of not more than 0.001%. The lime and silica required to form wollastonite were intimately mixed, and the batch was heated in a platinum crucible at 1600°C. (2910°F.) for one hour. The crucible containing the viscous melt was quenched in water.

The second mix containing iron was of wollastonite with the addition of 1.0% of Fe_2O_3. Because of the urgency of time, an available sample of Fe_2O_3 was used, which was believed to be quite pure. Analysis, however, showed later that the material was of poor quality, containing only 86.2% of Fe_2O_3 and having a silica content of 6.6% with 4.3% ignition loss. Unfortunately, the mixes containing iron were therefore not of the composition planned; nevertheless, these

[13] T. V. Memnonova and L. M. Zil'berfarb, "Spottiness of Silica Brick," *Ogneupory*, **5** [9] 613–15 (1937); *Ceram. Abs.*, **18** [3] 77 (1939).

[14] R. E. Birch, "Phase-Equilibrium Data in Manufacture of Refractories," *Jour. Amer. Ceram. Soc.*, **24** [9] 271–80 (1941).

mixes, for the sake of convenience, will be referred to as containing 1.0% of Fe_2O_3 rather than, in reality, a content of 0.90%. The silica content of the mixes containing iron, furthermore, will be about 0.07% higher than planned. The intimate mixture of the ingredients was heated in a platinum crucible to 1550°C. (2820°F.) for ½ hour and quenched in water.

The third mix was the same as the second except that 1.0% of alumina (99.1% of Al_2O_3) was added. This mixture was also heated in a platinum crucible at 1550°C. (2820°F.), but because the melt had sufficient fluidity, it was quenched by pouring it into water.

The three preparations were crushed to pass a 14-mesh sieve, and samples of each were heat-treated at three temperatures. The heating was carried out in porcelain crucibles except for the 1400°C. (2550°F.) trial in which platinum was used. A sample of each material was included in the heat-treatments carried out at 900°C. (1650°F.) and 1000°C. (1830°F.). The duration of the heating was 48 hours, after which time the crucibles were removed from the furnace, and the samples were allowed to cool quickly in the atmosphere. The treatment at 1400°C. (2550°F.) was for 2 hours' duration, and the samples were also cooled in the atmosphere.

The color of the three types of material as prepared and after the changes which developed through heat-treatment are presented in the color plate of Fig. 8. Comments on the appearance of these samples, as taken from the original materials, are as follows:

The wollastonite as prepared was pure white. The heat-treatments at 900°C. (1650°F.) and 1000°C. (1830°F.) produced only the slightest tinge of yellow-brown, whereas the heat-treatment at 1400°C. (2550°F.) caused a very slight gray tinge to occur.

The wollastonite mix with iron as originally prepared was a neutral slate-gray color, but after heat-treatment at 900°C. (1650°F.) it was a lighter and yellow-brown color. The 1000°C. (1830°F.) heating caused it to darken to a gray having a slight reddish tinge; after being heated to 1400°C. (2550°F.), it was a neutral gray but of an appreciably lighter shade than the color of the unheated material.

The wollastonite mix containing both iron and alumina was glassy and was a light aquamarine color. After treating this mix at 900°C. (1650°F.), a change to a yellow-brown occurred; and after 1000°C. (1830°F.) the color was a reddish brown, quite typical of the color of mottled brick. On continuing the heat-treatment to 1400°C. (2550°F.), it changed to a light yellowish gray.

By way of summary, it is shown that rather pure wollastonite, that is, containing only the smallest traces of iron, will show signs of color change with suitable heat-treatment. The wollastonite mix plus 1.0% of Fe_2O_3 (actually 0.90%), but without alumina, is a strongly colored product, and although heat-treatment causes changes to occur, they do not necessarily parallel in behavior those of silica brick. The wollastonite mix containing both iron and alumina closely approaches the behavior of silica refractories.

If time had permitted the 1400°C. (2550°F.) treatment to be carried for a longer period, the resulting color might have been a lighter shade judging from the effect of time during heating as shown in earlier portions of the work. When allowances are made for the way in which these samples were prepared and the short duration of the heat-treatment, which may not have brought about equilibrium, the color changes which took place in the wollastonite-iron mix as compared with such a mix containing alumina apparently indicate that alumina is an important constituent in the color-forming process or in the formation of the actual iron-bearing mineral.

It is interesting to note that approximately 1.0% of iron in the wollastonite mix is sufficient to cause the development of dark colors. This behavior shows that small percentages of iron in a silica brick could cause coloring because the total amount of wollastonite that would be present is of a relatively small order.

IV. Conclusions

(1) The properties of silica refractories cannot be judged by the color of the product, which has been shown by the complete series of tests used in comparing properties of both the light and colored products.

(2) The mottled areas of the silica brick can be changed to the typical light cream color of the product by heat-treatment. The light-colored areas of the same brick, furthermore, may be converted to the dark color by heating. Any silica brick apparently can be darkened in color by heating for a sufficiently long time at a suitable temperature.

(3) A slow rate of cooling heated brick is required to develop the color, and the normal cream color results when such brick are cooled at a fast rate.

(4) Sulfur does not appear to be a factor in color formation other than through the possibility of forming the more soluble calcium sulfate during the drying operation.

(5) An extremely small variation in the composition of a brick, which has no practical significance, may account for the color development in the mottled area (the light-colored area can be changed to the same color by heating).

(6) Microscopic examination indicates that the color-forming process proceeds through the development of wollastonite that may contain iron in solid solution which separates from it with heat-treatment, forming an iron-bearing mineral that is strongly colored.

(7) Experimental work with wollastonite mixes containing small quantities of iron and alumina indicates that only a small amount of iron is needed to cause color changes and that alumina appears to be necessary in the process in order to develop the colors which occur in mottled brick.

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NOTE ON ANOMALOUS HEAT ABSORPTION OF KAOLINITE*

By F. H. Norton and W G. Lawrence

Abstract

The unusually great heat absorption of certain sizes of kaolinite particles is described. There are indications that kaolinite may be a mixture of two similar minerals, one requiring more energy to drive off combined water.

During the last few years while making thermal curves of kaolins, it has been noted that the heat required to drive off the chemically combined water in a number of instances has been considerably greater than that determined for the pure kaolinite mineral. This has been especially true in certain size ranges. An excellent series of monodisperse fractions of the relatively pure Florida kaolin has been prepared recently in these laboratories. The size ranges of these fractions are shown in Fig. 1, and everything possible was done to purify them by the removal of organic matter, soluble salts, and adsorbed ions. A thorough X-ray petrographic study of the fractions indicated that all were kaolinite except the fraction 2, which contained 5% of quartz and mica, and fraction 1, which contained 10% of quartz and mica.

Thermal curves were run for each fraction, using a constant weight and volume of material, and the area of the absorption peak was plotted against the mean spherical diameter (Fig. 2). A regular curve was obtained having a peak at 2 microns. Fractions 1 and 2 have been corrected for the inert matter, and point *A* represents the value obtained on pure kaolinite crystals from Ione, Calif., which had been ground approximately to 100 microns in size. The fraction, 2 microns in size, is shown to require in excess of 50% more heat to drive off the combined water than that for pure kaolinite crystals. This is far beyond any experimental error and must be caused by some variation in the crystal itself.

To throw further light on the subject, the amount of combined water was determined from each fraction by ignition, and the results are plotted in Fig. 2. Correcting again for quartz and mica in the two coarser fractions, a curve is obtained that is quite similar in shape to that for heat absorption. Only a few percentage of variation, however, occurs in combined water, which will not explain the large variation in heat absorption.

A number of explanations are possible for this peculiar behavior of kaolinite, but none is completely satisfactory. It is hoped that as information on kaolinite and associated minerals increases a definite cause may be assigned to this phenomenon.

One of the plausible explanations is that certain size ranges include a proportion of a mineral having a higher water content than kaolinite, such as gibbsite or diaspore. To account for the observed change, however, such minerals would have to occur in comparatively large quantities, perhaps of the order of 30%; and, although the thermal method is sufficiently sensitive to detect as little as 1% of these minerals, none was indicated. The curve of combined water shows a peak at about the same point as the heat absorption, but it is not sufficiently large to account for any amount of this type of mineral.

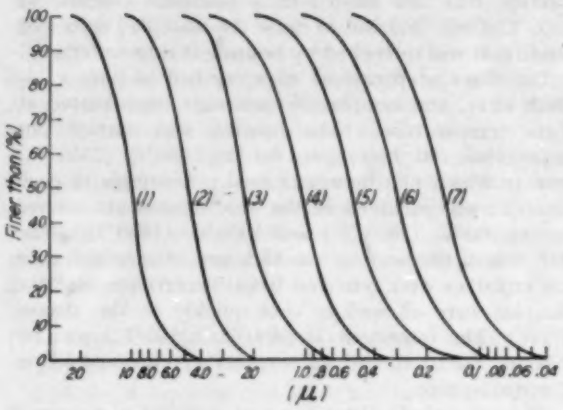

Fig. 1.—Size ranges of monodisperse fractions of Florida kaolin.

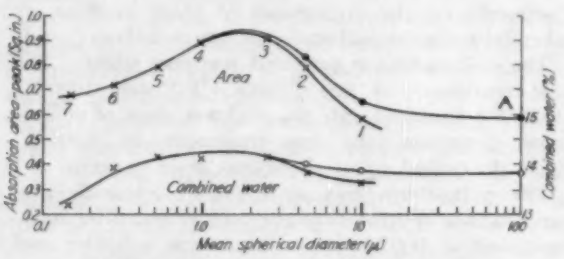

Fig. 2.—Area of absorption peak plotted against mean spherical diameter for each fraction.

These results might also be explained possibly by a variation in the physical properties of the specimens with particle size, such as diffusivity, which would permit a relatively higher temperature to be developed in the test sample in some cases. All of the fractions, however, had approximately the same porosity and were packed to the same density so that this explanation apparently cannot be valid.

The decrease in heat absorption in the very fine sizes might readily be explained by the presence of inert material with the kaolinite, but this explanation breaks down when consideration is given to the fact that the

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medium fractions have a heat absorption much greater than that of the pure crystalline kaolinite.

Ions are adsorbed on the surface of the kaolinite particles, and the majority of them are believed to be adsorbed on the broken edges and corners. In these particular fractions, the adsorbed ions are replaced by hydrogen; and as the fractions become finer, the surface increases enormously and the heat required to drive off the adsorbed hydrogen might be expected to increase the thermal effect. The maximum thermal effect, however, occurs at moderate sizes where the surface area is relatively low so that this explanation does not seem logical.

One other explanation is that the mineral known as kaolinite in reality may be a mixture of two similar minerals that cannot be differentiated. If one of them required more thermal energy to drive off the combined water than the other and if this particular mineral occurred more plentifully in the fractions around the 2-micron size, the behavior could be readily explained.

The writers hope that this brief note will serve to stimulate thought on the constitution of kaolinite and ultimately lead to an explanation of this perplexing phenomenon.

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POSSIBLE USE OF FERRUGINOUS TALCS IN STEATITE DIELECTRICS*

By Laurence E. Kane and Herbert G. Ueltz

Abstract

Several iron-bearing talcs were fired alone and in body form and were measured for shrinkage and absorption. Their colors were also noted. Electrical measurements of dielectric constant and loss characteristics were made on the bodies and compared with white-firing talcs. The effect of small additions of Fe_2O_3 on a white-firing talc is also described.

I. Introduction

Associated with many of the domestic talcs are small or moderate amounts of iron occurring as magnetite, chlorite, pyrrhotite, actinolite, and staining films of the iron oxides. These iron-bearing minerals impart a color ranging from a light buff to a deep chocolate-brown to the fired steatite bodies when they are fired under oxidizing conditions. Aside from this coloring effect, which may be objectionable, the question arises as to whether the use of some ferruginous talcs would be detrimental to the firing and electrical properties of steatite.

II. Experimental Procedure

(1) Series A

A comparison of talcs alone was made after firing to cone 10. Seven ferruginous talcs and six white-firing talcs were used, whose analyses appear in Table I. The first seven talcs have a relatively high iron content and the next six are low in iron. The Manchurian talc was employed in a subsequent series.

The talcs were wet ground in small ball mills with 2% of a soluble urea resin and hardener. The resulting slip was dried in an electric drier and crushed in a mortar. The material was then prepared for dry pressing by adding 8% of moisture and screening through a 20-mesh sieve.

Disks were pressed using a pressure of 5000 lb. per sq. in., the disk size being approximately 2 in. in diameter and 100 to 130 mils thick. After drying, the disks were fired to cone 10 (approximately 1260°C.), and the temperature was maintained for one hour at that point. The heating rate during firing was about 300°F. per hour.

Water-absorption tests were made on the resulting disks to determine the relative vitrification. This was done in accordance with A.S.T.M. designation D116–39 except that three samples instead of five were tested. The colors were also noted, and the total shrinkage was calculated after measuring the diameters of the dry-pressed and fired disks.

(2) Series B

The effect of beneficiating a talc was determined. One talc was employed in these tests, samples being made from the unwashed and washed material (see Alabama No. 1 and Alabama No. 2 in Table I). Disks were pressed as in series A, but 30% of a barium silicate glass was needed to produce vitreous bodies suitable for electrical testing. This glass was produced by fusing a mixture of 47% of BaO and 53% of SiO_2 and pouring the melted material into water. After drying, this frit was ground in a ball mill to pass a 325-mesh sieve. The shrinkages and absorptions of these bodies were taken after firing to cones 10 and 12 and electrical properties were determined at room temperature.

The fired samples were prepared for electrical testing by rubbing a thin film of boiled petroleum jelly on the surfaces and covering with tin-foil electrodes. Electrical measurements were made on series B and series C with a type 100-A Q meter. Dielectric constant, power factor, and dielectric-loss factor were calculated from the data obtained. The color of the fired samples was also noted.

(3) Series C

The same talcs were used as those in series A except that they were now incorporated in vitreous steatite

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TABLE I

CHEMICAL ANALYSES OF TALCS

Talc	SiO_2	MgO	Iron oxide	R_2O_3	CaO	Na_2O	CO_2	Loss
				Ferruginous talcs				
Ala. No. 1	59.5	27.2	3.6 (Fe_2O_3)	3.5 (Al_2O_3)	0.2			5.9
Md.	56.3		3.36 (Fe)	10.4	0.43			6.00
Ga.	57.19	27.70	6.30	2.19 ($Al_2O_3 + TiO_2$)	None found			4.80
Soapstone			Approx. 4.00 (Fe_2O_3)		(Analysis not available)			
Vt. No. 1	60.4	30.17	2.05 (Fe)	6.0	Trace			4.60
Vt. No. 2			6.26 (FeO)		(Analysis not available)			
Vt. No. 3	56.56	30.61	3.83 (Fe_2O_3)	0.78 (Al_2O_3)			3.26	4.89
				White-firing talcs				
Ala. No. 2	63.6	29.2	0.7 (Fe_2O_3)	1.6 (Al_2O_3)	0.1			4.89
N. Y. No. 1	56.72	30.81		0.70 (0.17 B_2O_3)	4.80	0.50		5.95
N. Y. No. 2	56.17	30.52	0.20 (Fe_2O_3)	1.40	6.42			5.20
Calif. No. 1	62.8	28.6	0.42 (Fe)	3.8	0.82			4.10
Calif. No. 2	63.4	27.6	0.32 (Fe)	1.5	2.55			2.70
Calif. No. 3	59.7	30.5		1.2				7.0
				Manchurian talc (D series)				
	61.20	30.35	Fe oxide—1.40—Al_2O_3		0.85			3.30

bodies. Disk samples were pressed from all the talcs used in series A. The body mix consisted of 77.5% of talc, 17.5% of ball clay, and 5% of the barium silicate glass previously described. The samples were prepared as in series A and were fired to cone $12^1/_2$ (approximately 1330°C.), the temperature at this point being maintained for one hour. The bodies were highly vitrified after firing. The shrinkage, absorption, and electrical data at room temperature were taken, and the colors were noted.

(4) Series D

The effects of adding small amounts of Fe_2O_3 in a steatite body are demonstrated. Four bodies were prepared as previously described; their compositions are given in Table II. The Fe_2O_3 was substituted in progressive increments for the relatively iron-free Manchurian talc, thereby simulating a series of ferruginous talcs varying only in iron content. All of the samples were fired to cone $12^1/_2$ and were vitreous. The absorptions, shrinkages, and colors were noted.

Electrical tests on these samples were made at the Bell Telephone Laboratories, Murray Hill, N. J. The samples were prepared for these tests as follows: Silver electrodes were applied to the samples using No. 28 Hanovia silver paste, which was fired on at 750°C. Using a type 160-A Q meter, measurements of dielectric loss were made at 100-, 300-, and 1000-kc. frequencies and at 25°, 250°, 350°, and 450°C. The dielectric constant was determined at room temperature from the measured capacitance, corrected for edge effect and stray capacitance to ground.

TABLE II

COMPOSITIONS OF SERIES D

Sample No.	Manchurian talc (%)	Fe_2O_3 (%)	Barium silicate glass (%)
0	70	0	30
1	69	1	30
2	68	2	30
3	67	3	30

III. Results

The results are given in Tables III through VII and in Figs. 1 through 3.

(1) Series A

Two firing effects characteristic of iron-bearing talcs are shown in Table III. First, the absorptions

TABLE III

SERIES A TALCS AT CONE 10

Talc	Total shrinkage (%)	Absorption (%)	Color
Ala. No. 1	13.32	1.11	Tan
Md.	3.09	14.25	Dark brown
Ga.	3.28	16.82	Brown
Soapstone	3.60	10.08	"
Vt. No. 1	3.28	13.27	"
Vt. No. 2	4.16	18.43	"
Vt. No. 3	3.05	13.39	"
Avg.	4.83	12.48	
Ala. No. 2	2.51	19.72	White
N. Y. No. 1	2.90	20.84	"
N. Y. No. 2	3.28	19.31	"
Calif. No. 1	4.25	13.57	Cream
Calif. No. 2	3.09	18.31	White
Calif. No. 3	4.83	11.71	Cream
Avg.	3.48	17.24	

TABLE IV

DATA ON SERIES B

Talc	Absorption (%)	Shrinkage (%)	Dielectric constant (K)	Power factor (%)	Loss factor (%)	Color
			Cone 10 bodies			
Unwashed	0.10	12.03	5.86	0.244	1.426	Tan
Washed	5.93	8.12	5.20	0.204	1.059	Off-white
			Cone 12 bodies			
Unwashed	0.10	12.61	5.62	0.348	1.96	Tan
Washed	1.36	9.53	5.60	0.174	0.974	Off-white

TABLE V

SERIES C AT CONE 12½

Talc	Absorption (%)	Shrinkage (%)	Dielectric loss (K)	Power factor (%)	Loss factor (%)	Color
Ala. No. 1	0.07	10.22	5.64	0.388	2.19	Brown
Md.	0.21	5.67	5.88	1.60	9.41	Dark brown
Ga.	0.09	7.75	5.78	0.389	2.25	Deep tan
Soapstone	0.14	6.24	6.15	0.445	2.74	Dark brown
Vt. No. 1	0.15	7.81	5.88	0.280	1.65	Tan
Vt. No. 2	0.84	11.70	6.77	0.836	5.66	Dark brown
Vt. No. 3	0.12	7.02	5.47	0.477	2.61	Brown
Avg.	0.23	8.06	5.94	0.631	3.79	
Ala. No. 2	0.07	9.72	5.49	0.205	1.13	White
N. Y. No. 1	0.22	8.09	6.17	0.162	1.00	"
N. Y. No. 2	1.38	9.13	6.00	0.138	0.828	"
Calif. No. 1	0.12	7.61	5.71	0.222	1.27	Off-white
Calif. No. 2	0.21	8.44	6.01	0.155	0.932	White
Calif. No. 3	0.15	8.67	5.65	0.248	1.40	Off-white
Avg.	0.34	8.53	5.84	0.188	1.09	

are lower and the shrinkages higher in the case of the ferruginous talcs, showing that the iron presumably exerts some fluxing action. Second, the color of the iron-bearing talcs is a brown of varying shades. This color is almost directly proportional to the iron content for the lower percentages of iron, and if no other coloring oxides are present, the color enables a rough estimate of the iron content to be made.

(2) Series B

Table IV shows the effects of washing out certain impurities from a talc. Among these impurities is most of the iron.

At cone 10, the unwashed talc produced a vitreous body whereas the washed talc produced a more refractory body. Although electrical data were taken on both bodies, the washed talc body results may be somewhat in error because of its porosity. The data show that the iron and other impurities gave a slightly higher dielectric constant, power factor, and loss factor. The washing process removed enough iron to give a nearly white-firing talc.

At cone 12, both bodies were nearly vitreous and more suitable for electrical testing. The fluxing effect of the iron oxide is again noted The electrical tests show that the unbeneficiated talc was characterized in body form by a slightly higher dielectric constant and a somewhat higher power factor.

(3) Series C

The use of ferruginous talcs in this series of bodies produced satisfactory samples similar to those made from the white-firing talcs except in color (see Table V). The iron apparently exerted a mild fluxing action as seen from the slightly lowered absorption.

The power factor of the iron-bearing bodies, in general, is somewhat higher than that of the white bodies, and the higher percentages of iron may have an appreciable effect on this factor.

(4) Series D

The effect of small additions of Fe_2O_3 on the firing properties of the samples in series D showed progressively darker brown color and slightly lower absorption with increasing iron content as would be expected (see Table VI).

TABLE VI

SERIES D, ABSORPTION, SHRINKAGE, COLOR

Sample No.	Absorption (%)	Total shrinkage (%)	Color
0	1.10	6.76	White
1	0.65	8.11	Light buff
2	0.36	10.00	Tan
3	0.59	10.60	Brown

Figure 1 shows that at 100 kc. the iron caused only a slight detrimental effect on the tangent of the loss angle at 25°C., but this effect was much more pronounced at elevated temperatures.

At 300 kc., the same effect of iron oxide in the steatite body is noted as at 100 kc., but it is less severe (Fig. 2). Higher temperatures cause less marked effect at this frequency. At 25°C., little difference is observed between bodies 0 and 3 in respect to the dielectric loss.

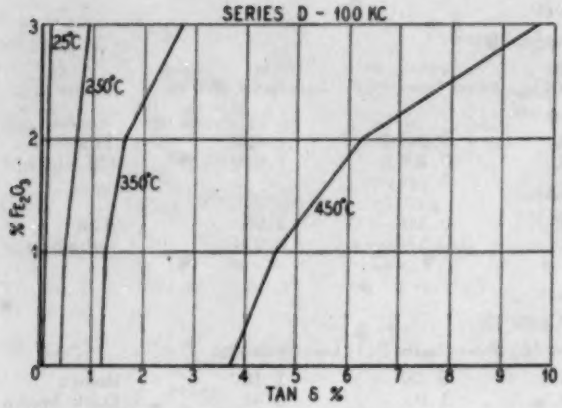

FIG. 1.—Effect of iron on the tangent of loss angle at 100 kc. and at varying temperatures.

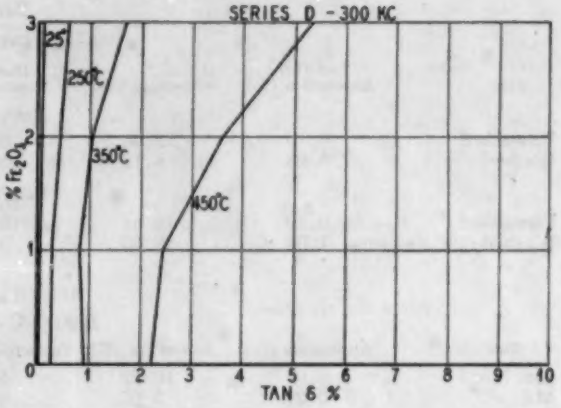

FIG. 2.—Effect of iron on the tangent of loss angle at 300 kc. and at varying temperatures.

At 1000 kc., the effect is greatly diminished and the curves tend more nearly to parallel themselves (see Fig. 3). Practically no effect can be seen at 25°C.

At 25°C., the dielectric constant was raised slightly by the addition of Fe_2O_3 in the given amounts (Table VII).

TABLE VII

EFFECT OF SMALL PERCENTAGE OF Fe_2O_3 ON DIELECTRIC CONSTANT OF A STEATITE BODY AT 25°C.*

	Fe_2O_3 (%)			
Frequency (kc.)	0	1	2	3
1000	5.88	6.02	6.04	6.04
300	5.89	5.99	5.90	5.93
100	5.87	5.95	5.97	6.04

* Avg. of 3 values.

IV. General Conclusions

(1) Low percentages of iron in a steatite body act as a mild flux. This conclusion is presumably true for most steatite bodies.

(2) When fired under oxidizing conditions, iron oxide imparts a brownish color to the fired steatite body which varies almost directly with the iron content within limits.

(3) Beneficiation of talc may be used to remove iron, and the resulting material may produce a satisfactory steatite body.

(4) Small amounts of ferric oxide exert little or no detrimental effect on the dielectric properties of a steatite body, especially at higher frequencies and low temperatures.

(5) Iron impurities in larger amounts give an increased power factor and a slightly increased dielectric constant. The effect on the dielectric loss becomes

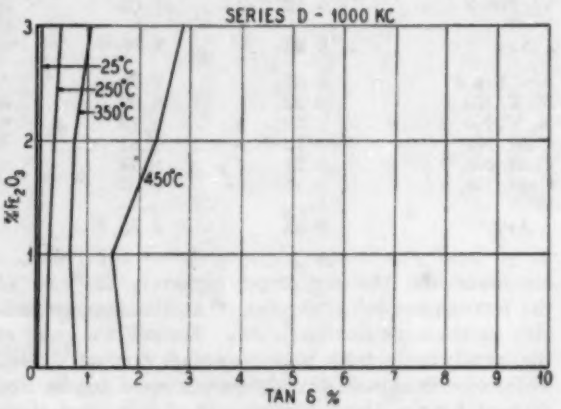

FIG. 3.—Effect of iron on the tangent of loss angle at 1000 kc. and at varying temperatures.

especially marked at low frequencies and high temperatures.

(6) Within limits, certain ferruginous talcs may be used in steatite dielectrics without serious detriment, other than that of uniform coloration, on either the firing or electrical properties if oxidizing conditions are maintained during firing.

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